Final Report

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Novel Sorbent-Based Process for High Temperature Trace Metal Removal

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Disclaimer

1. Executive Summary

The objective of this project was to demonstrate the efficacy of a novel sorbent can effectively remove trace metal contaminants (Hg, As, Se and Cd) from actual coal-derived synthesis gas streams at high temperature (above the dew point of the gas). The performance of TDA's sorbent has been evaluated in several field demonstrations using synthesis gas generated by laboratory and pilot-scale coal gasifiers in a state-of-the-art test skid that houses the absorbent and all auxiliary equipment for monitoring and data logging of critical operating parameters. The test skid was originally designed to treat 10,000 SCFH gas at 250 psig and 350^{o}C, however, because of the limited gas handling capabilities of the test sites, the capacity was downsized to 500 SCFH gas flow.

As part of the test program, we carried out four demonstrations at two different sites using the synthesis gas generated by the gasification of various lignites and a bituminous coal. Two of these tests were conducted at the Power Systems Demonstration Facility (PSDF) in Wilsonville, Alabama; a Falkirk (North Dakota) lignite and a high sodium lignite (the PSDF operator Southern Company did not disclose the source of this lignite) were used as the feedstock. We also carried out two other demonstrations in collaboration with the University of North Dakota Energy Environmental Research Center (UNDEERC) using synthesis gas slipstreams generated by the gasification of Sufco (Utah) bituminous coal and Oak Hills (Texas) lignite.

In the PSDF tests, we showed successful operation of the test system at the conditions of interest and showed the efficacy of sorbent in removing the mercury from synthesis gas. In Test Campaign# 1, TDA sorbent reduced Hg concentration of the synthesis gas to less than 5 $\mu g/m^3$ and achieved over 99% Hg removal efficiency for the entire test duration. Unfortunately, due to the relatively low concentration of the trace metals in the lignite feed and as a result of the intermittent operation of the PSDF gasifier (due to the difficulties in the handling of the low quality lignite), only a small fraction of the sorbent capacity was utilized (we measured a mercury capacity of 3.27 mg/kg, which is only a fraction of the 680 mg/kg Hg capacity measured for the same sorbent used at our bench-scale evaluations at TDA). Post reaction examination of the sorbent by chemical analysis also indicated some removal As and Se (we did not detect any significant amounts of Cd in the synthesis gas or over the sorbent).

The tests at UNDEERC was more successful and showed clearly that the TDA sorbent can effectively remove Hg and other trace metals (As and Se) at high temperature. The on-line gas measurements carried out by TDA and UNDEERC separately showed that TDA sorbent can achieve greater than 95% Hg removal efficiency at 260^{o}C (~200g sorbent treated more than 15,000 SCF synthesis gas). Chemical analysis conducted following the tests also showed modest amounts of As and Se accumulation in the sorbent bed (the test durations were still short to show higher capacities to these contaminants).

We also evaluated the stability of the sorbent and the fate of mercury (the most volatile and unstable of the trace metal compounds). The Synthetic Ground Water Leaching Procedure Test carried out by an independent environmental laboratory showed that the mercury will remain on the sorbent once the sorbent is disposed.

Based on a preliminary engineering and cost analysis, TDA estimated the cost of mercury removal from coal-derived synthesis gas as $2,995/lb (this analysis assumes that this cost also includes the cost of removal of all other trace metal contaminants). The projected cost will result in a small increase (less than 1%) in the cost of energy.

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List of Acronyms

As – Arsenic
AsH_3 – Arsine (or arsenic hydride)
ASME – American Society of Mechanical Engineers
CEM – Continuous Emission Monitor
Cd - Cadmium
CFBR – Continuous Fluidized-bed Reactor
CO – Carbon monoxide
CO_2 – Carbon dioxide
COS – Carbonyl sulfide
CuO – Copper oxide
DI – De-ionized
GC – Gas chromatograph
GHSV - Gas hourly space velocity
H_2 – Hydrogen
H_2O – Water
H_2S – Hydrogen sulfide
H_2Se – Hydrogen selenide
Hg – Mercury
HGFV – Hot gas filter vessel
ICP-AA – Inductively Coupled Atomic Absorption
IGCC – Integrated Gasification Combined Cycle
O&M – Operating and Maintenance
P&ID – Process and Instrumentation Diagram
PSDF – Power Systems Demonstration Facility
Rpm – rounds per minute
RTI – Research Triangle Institute
SBIR – Small Business Innovative Research
SCFM – Standard Cubic Feet per Minute
SCF – Standard Cubic Feet
SCFH – Standard Cubic Feet per Hour
SGLP – Synthetic Groundwater Leaching Potential
SS – Stainless steel
TCLP – Toxic Contaminant Leaching Potential
TRDU – Transport Reactor Demonstration Unit
UNDEERC – University of North Dakota Energy and Environmental Research Center
WGS – Water gas shift
XRF – X-ray Flouresence
ZnO – Zinc Oxide

2. Project Summary

Gasification technologies convert coal and other heavy feedstocks into synthesis gas feed streams that can either be used as a fuel for highly efficient power generation cycles or converted into value-added chemicals and transportation fuels. However, coal-derived synthesis gas contains a myriad of trace contaminants (e.g. mercury, arsenic, selenium) that may be regulated in power plant emissions and act as poisons for fuel cells or the catalysts used in downstream chemical manufacturing processes. The objective of this project is to demonstrate a chemical absorbent-based process to remove all trace metal contaminants (including mercury, arsenic, selenium and cadmium) from coal-derived synthesis gas at high temperatures (260^{o}C) in a single process step. High temperature removal of these contaminants greatly improves the overall efficiency of the power cycle because cold gas clean-up systems condenses the steam in the synthesis gas , reducing the power cycle efficiency by roughly 10% on relative basis.

In two Small Business Innovative Research (SBIR) Phase II projects ("Sorbents for Mercury Removal from Coal Gasifier Effluents" Grant No. DE-FG03-02ER83551 and "Control of Catalyst Poisons from Coal Gasifiers" Grant No. DE-FG03-01ER83308), TDA Research, Inc. developed a high temperature sorbent for removing catalyst poisons (e.g., arsenic, selenium) and criteria air pollutants (e.g., mercury) from coal-derived synthesis gas at high temperatures. TDA's sorbent contains a highly active absorbent to remove these contaminants via a chemical interaction (e.g., forming a covalent bond). Therefore, unlike the commercially available sorbents that physically adsorb mercury and must be operated at near ambient temperatures, our sorbent operates at elevated temperatures and removes these metals by forming chemical complexes and amalgamates. In the SBIR projects, we already demonstrated technical viability of the concept at the bench-scale using simulated synthesis gas under representative conditions. We also showed that the sorbent can achieve an exceptionally high absorption capacity for mercury, arsenic and selenium and can remove multiple trace contaminants from simulated coal gas in a single step. We also subcontracted with Saint Gobain NorPro, a leading U.S. sorbent manufacturer, to produce the sorbent using commercial manufacturing techniques. Under subcontract to TDA, NorPro delivered 100 lb of sorbent using its proprietary pellet forming technology based on our preparation recipe. Bench-scale experiments confirmed that the performance capabilities of the NorPro made sorbent matched those prepared by TDA.

The primary objective of this project was to prove that this novel sorbent can effectively remove these trace metal contaminants (Hg, As, Se and Cd) from actual coal-derived synthesis gas streams produced by different coals and gasifiers. The proof-of-concept tests were carried out in several field demonstrations using the synthesis gas generated by laboratory and pilot-scale coal gasifiers. For the evaluations, we built a state-of-the-art test skid that houses the absorber and all auxiliary equipment for monitoring and data logging of critical operating parameters. This prototype unit was originally designed to treat 10,000 SCFH coal-derived synthesis gas at up to 250 psig and 350^{o}C (the selected capacity represented a 250-fold increase from the bench-scale experiments). However, because of the limited gas handling capabilities of the test sites, the skid capacity was downsized to 500 SCFH gas flow. The prototype test skid contained three sorbent reactors capable of evaluating sorbent performance at different operating conditions (e.g., 150-350^{o}C, 15-250 psig).

As part of the test program, we carried out four demonstrations at two different sites using the synthesis gas generated by the gasification of various lignites and a bituminous coal. Two of

these tests were conducted at the Power Systems Demonstration Facility (PSDF) in Wilsonville, Alabama; a Falkirk (North Dakota) lignite and a high sodium lignite (the PSDF operator Southern Company did not disclose the source of this lignite) were used as the feedstock. In collaboration with the University of North Dakota Energy Environmental Research Center (UNDEERC), we also carried out two more demonstrations using synthesis gas slipstreams generated by the gasification of Sufco (Utah) bituminous coal and Oak Hills (Texas) lignite. A summary of these demonstrations are provided in Table 1.

Table 1. Summary of the demonstration tests.

Campaign	Coal Type	Sorbent Used (g)		Time On-stream (h)		Syngas Treated (SCF)		Hg Removal Efficiency
		Bed A	Bed B	Bed A	Bed B	Bed A	Bed B	
PSDF #1	Falkirk lignite (North Dakota)	480	480	53.3	42.4	40,940	14,020	95+%
PSDF #2	High Sodium Lignite	126	126	161.8	NA	28,670	NA	NA
UNDEERC #1	Sufco Bituminous (Utah)	203	203	30.4	21.9	15,001	10,819	90+%
UNDEERC #2	Oak Hills Lignite (Texas)	203	203	45.5	34.3	12,723	9,751	95+%

Overall, the test results suggested that TDA sorbent is capable of removing multi-contaminants in the coal-derived synthesis gas at high temperature using the synthesis gas streams generated by different gasifiers using different coals at different sites. The on-line gas measurements by TDA and UNDEERC also showed that TDA sorbent can achieve greater than 95% Hg removal efficiency at 260^{o}C. Finally, we showed that TDA sorbent can be operated in a regenerable manner to remove Hg from the bed; Hg in the regeneration gases is then captured on another sorbent bed operated at a low temperature achieving a higher Hg capacity. The regeneration conditions were relatively mild and no release of other contaminants (i.e., As and Se) were observed.

2.1 Summary of the Demonstration Tests at Power Systems Demonstration Facility (PSDF)

As part of our work at the PSDF, our objective was to develop an understanding and knowledge base on our novel trace metal removal sorbent and gas clean-up process, and confirm its performance capabilities while treating actual coal-derived synthesis gas. These tests were conducted as part of a different lignite gasification project undertaken by the PSDF operator, Southern Company. TDA tests were piggy-backed on the testing being conducted at the PSDF and TDA (or this DOE project) did not pay for the operation of the gasifier. It was Southern Company's objective to evaluate the suitability of some of the low cost and low quality lignites in their gasifier. Both gasification campaigns at PSDF were originally scheduled to last for 3 weeks, however, through the course of these gasification campaigns, it was found to be difficult to feed the selected lignites to the gasifier, causing unscheduled gasifier shutdowns due to problems encountered in the coal feeder, which eventually led to the pre-mature termination of both tests.

In both demonstrations, our plan was to maintain sorbent bed temperature above 260^{o}C to demonstrate the high temperature contaminant removal capability. In both test campaigns, a small fraction of the synthesis gas produced by the Transport Gasifier was run through TDA Test Skid which is located downstream of a hot gas particulate control system, an activated alumina type commercial carbonyl sulfide (COS) hydrolysis catalyst bed (converting COS to hydrogen sulfide, H_2S) and a ZnO (zinc oxide)-based commercial desulfurization sorbent bed to remove the H_2S. Southern Company did not disclose the product number, producers or any

other information related to the chemical composition of the COS hydrolysis catalyst and the desulfurization sorbent. In these tests, our test skid accepted synthesis gas flows to two sorbent reactors. One of the beds would be used to evaluate the regeneration potential of the sorbent. Throughout the first gasification campaign at PSDF, our test skid contained 960 g (480 g in each bed) sorbent, treated 54,960 SCF (40,940 SCF in Bed A and 14,020 SCF in Bed B) synthesis gas through the course of 96 hrs. The on-line measurements with a Continuous Emission Monitor (CEM) and gas analysis using bagged gas samples showed that the TDA sorbent can effectively remove Hg from the actual coal-derived synthesis gas with very high removal efficiency at 260°C (Figure 1). The sorbent reduced the Hg concentration in the synthesis gas from 1,400 ng/m^3 to less than 10 ng/m^3 (below the detection limit of the CEM), achieving greater than 95% Hg removal efficiency (the small spike in the 11/17/06 time frame is attributed to the Hg remaining in the gas sampling lines).

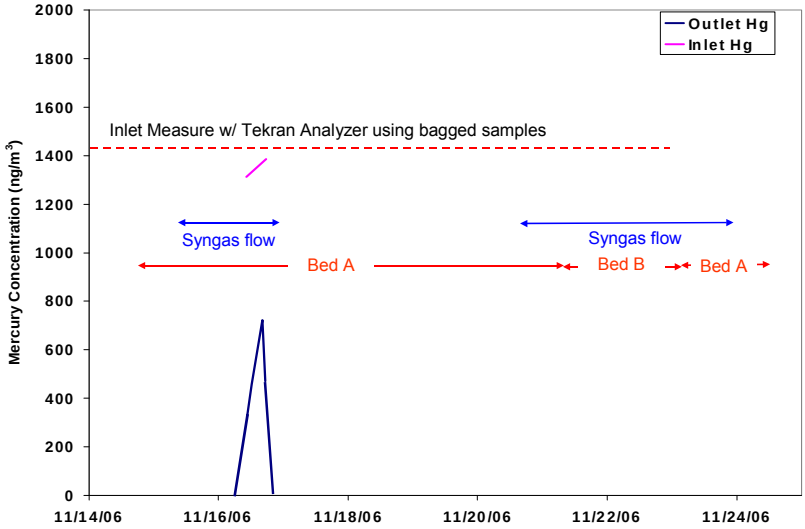

Figure 1. Hg concentration profiles at the inlet and the exit of the sorbent beds during the 1st test campaign at PSDF. T= 260°C.

Because we made a highly conservative selection for the sorbent bed size (designing the beds for longer operation with a synthesis gas containing higher concentration of Hg based on the elemental analysis provided by Southern Company), the sorbent beds were oversized. As a result, the calculated Hg capacity in these tests was not representative of the ultimate Hg capacity of the sorbent. We measured a mercury capacity of 3.27 mg/kg for Bed A and 1.12 mg/kg for Bed B, which were only a fraction of the 680 mg/kg Hg capacity measured for the same sorbent used at our bench-scale evaluations at TDA.

It was our intention to conduct on-line measurements for the gaseous hydrides of arsenic and selenium, arsenic hydride (AsH_3) and hydrogen selenide (H_2Se), however, due to the interference caused by sodium vapors and other condensable phases in the lignite-derived synthesis gas, TDA hydride analyzers did not work properly. Therefore, we evaluated the sorbent capacity for all other trace metals by carrying out chemical analysis on the sorbent particles removed from the bed after the demonstration test. The chemical analysis results showed the highest loadings observed at the samples removed from the inlet section of the bed as 18 mg/kg, 9 mg/kg and 7 mg/kg for arsenic, selenium and cadmium, respectively. As in the case of mercury, the measured sorbent capacity for these contaminants was only a small fraction of what we measured during the bench-scale tests at TDA, because of the short test duration, oversizing the test beds and the presence of these trace metal contaminants at very low concentrations of contaminants in the synthesis gas (much lower than expected).

The second test campaign at the PSDF was also shorter than originally planned. Because of the high sodium content of the lignite that was used for testing, the gasifier operation was highly unstable, and TDA test skid intermittently received 28,670 SCF synthesis gas over the course of

162 hrs (although the test duration was longer than the first test, the amount of gas received from the synthesis gas stream was lower due to the plugging of the flow valves). Only one of the sorbent beds was used during these tests. The temperature of the bed was maintained at 260°C. Based on our experience in the first campaign, we resized the sorbent reactors and reduced the amount of sorbent used in each sorbent bed from 480 g to 126 g in an effort to observe Hg breakthrough from the bed.

In the second test campaign, the two mercury CEMs provided in TDA's gas analysis rack malfunctioned because the sodium vapors covered the lamp and greatly reduced the signal intensity. As a result, all capacity measurements were carried out by post-reaction chemical analysis. We measured a Hg capacity of 4.04 mg/kg for the samples removed from the inlet section of the sorbent bed.

For As, Se and Cd, the chemical analysis results again showed the highest loadings at the samples removed from the inlet section of the bed. We measured 58.2 mg/kg, 17.2 mg/kg and 13.1 mg/kg for arsenic, selenium and cadmium, respectively. Because of the relatively longer test duration, higher contaminant levels in the high sodium lignite and a smaller amount of sorbent used in the bed, in the second test campaign at PSDF, we measured a higher capacity for the contaminants. However, as in the case of the first campaign, the measured capacity for these contaminants was only a small fraction of what we measured during the bench-scale tests at TDA because there was so little contaminant available for removal.

In the PSDF tests, using actual coal-derived synthesis gas generated by the gasification of two different types of lignites, we proved that the TDA sorbent developed in the SBIR projects funded by DOE can effectively remove mercury and other trace metals, while achieving a high removal efficiency at least for mercury at 260°C. Unfortunately, due to the numerous gasifier shutdowns and short durations allocated to access the synthesis gas, the data generated in these demonstrations did not reveal the ultimate capacity of the sorbent and the full potential of the gas clean-up technology. At the conclusion of the PSDF tests, DOE provided TDA with additional funding and granted an extension in the performance period to gain more information on the technology and evaluate the sorbent performance in additional field demonstrations.

2.2 Summary of the Demonstrations Tests at UNDEERC

In the extension of the project, TDA carried out two more demonstration tests at UNDEERC's Gasification Facility using a slipstream of coal-derived synthesis gas provided from their TRDU gasifier and continuous fluidized bed reactor (CFBR). Figure 2 shows the schematic of the gas

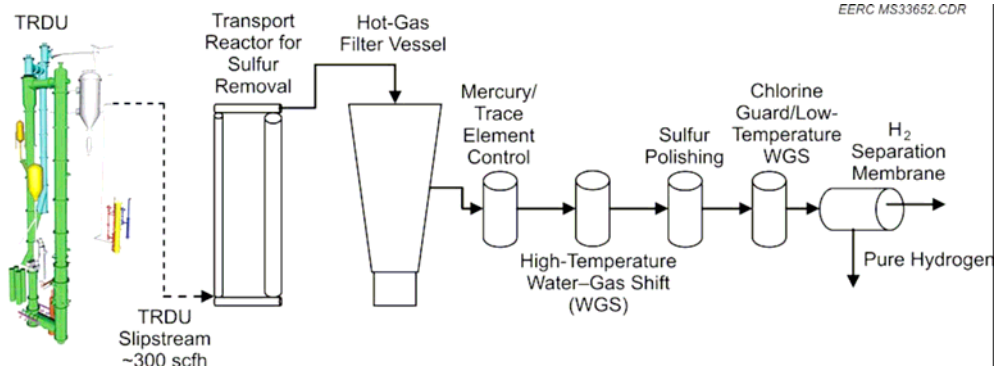

Figure 2. The schematic of the gas processing and clean-up train used at the gasification campaigns at UNDEERC.

clean-up and processing train where several warm-gas cleanup technologies were evaluated during the test campaign, including the TDA's skid for mercury and trace element control. All warm-gas cleanup procedures were performed at temperatures over 205°C, and TDA unit was operated at 235°C.

Table 1. The average mercury concentration at the inlet and the exit of the TDA test skid during the first gasification campaign at UNDEERC (data generated by UNDEERC).

Test No.	Hg Baseline, µg/m^3	Hg Concentration, µg/m^3	% Hg Removal
1	7.10	0.67	90.56
2	7.21	1.08	85.02
3	9.55	0.00	100.00
4	8.47	1.24	85.36
5	8.47	1.36	83.94
6	8.47	1.34	84.18
7	8.47	1.63	80.76
8	NA	NA	NA

In the first test campaign using Sufco (Utah) bituminous coal, the TDA test skid treated more than 25,820 SCF synthesis gas in the course of 52.3 hrs. In addition to the CEMs provided with the TDA Analyzer Rack, the mercury concentration of the synthesis gas at the inlet and exit of the TDA test skid was independently measured by UNDEERC to provide an independent assessment of sorbent performance. Table 1 shows the average mercury concentration at the inlet and exit of the TDA test skid during each of the test periods measured by UNDEERC. When the TDA unit was on-line, it achieved mercury removal efficiency ranging from 80-90%, maintaining the Hg concentration of the synthesis gas leaving the test skid below 1.7 µg/m^3 at all times. During Test Period 7 (about 40 hrs into the test), the warm gas desulfurization sorbent located upstream of our test skid failed, exposing the test skid to 2,000 ppmv of sulfur. The exposure of high levels of sulfur caused a significant degradation to the sorbent performance and testing had to be terminated. The TDA sorbent can tolerate low levels of sulfur (e.g., 0-10 ppmv) and should ideally be located downstream of a bulk desulfurization system. The sulfur in the synthesis gas interacts with the sorbent forming a stable sulfide. When present at low levels, the sulfur absorption does not impede sorbent's ability to remove trace metal contaminants (in fact, the sorbent does an excellent job as a multi-contaminant control bed polishing sulfur reducing its concentration to ppbv levels in addition to removing trace metals). However, when present at 2,000 ppmv, the sulfur rendered our sorbent inactive for trace metal removal. Post-reaction chemical analysis showed that the sulfur concentration in the bed was more than 2.4% wt. on average (higher at the bed inlet). Due to the limited test duration of the test campaign, the amount of metal accumulation in the sorbent bed was low.

In the second campaign (with the Oak Hills lignite), TDA test skid treated 22,474 SCF gas through the course of 79.8 hrs. While the TRDU had 16 scheduled test periods, there were only 10 test periods identified on the warm-gas cleanup end of the process, which were divided by changes in the process train flow (during the start-up and stabilization and shutdown of the gasifier, the TDA test skid and the whole gas clean-up and processing train did not receive any synthesis gas). Figure 3 shows mercury concentration

Table 2. The average mercury concentration at the inlet and the exit of the TDA test skid during the second gasification campaign at UNDEERC (data generated by UNDEERC).

Test No.	Hg Baseline, µg/m^3	Hg Concentration, µg/m^3	% Removal
1	NA	NA	TDA off-line
2	NA	NA	TDA off-line
3	21.5	0.31	98.56
4	21.5	0.075	99.65
5	21.5	0.018	99.92
6	41.8	1.13	97.30
7	54.7	54.7	TDA off-line
8	56.6	0.108	99.81
9	45.1	6.78	84.97
10	55.8	0.436	99.22

measured by UNDEERC CEM (confirmed by the CEMs at TDA Analyzer Rack) during Test 6 (longest duration) of the warm-gas cleanup process. When the TDA system was online, Hg concentration was maintained below 5 μg/m^3 at all times. When the system was off-line, Hg concentration increased dramatically to a baseline concentration of roughly 40–50 μg/m^3 (e.g., the Hg concentration at the inlet). Table 2 shows the average mercury concentration during each of the 10 test periods. This data is representative of the time during each test period when the TDA skid was online. The TDA skid was closed to flow during Tests 1, 2, and 7, but during the other test periods, mercury removal ranged from 97.3%–99.9%. Test 9 was lower than this range because the TDA skid was only online for a short time during this period and did not reach steady state before being taken off-line. These results shows that the TDA skid was capable of removing Hg very effectively with very high efficiency from actual coal-derived synthesis gas provided by a pilot-scale transport gasifier. Appendix A provides the details of the UNDEERC results.

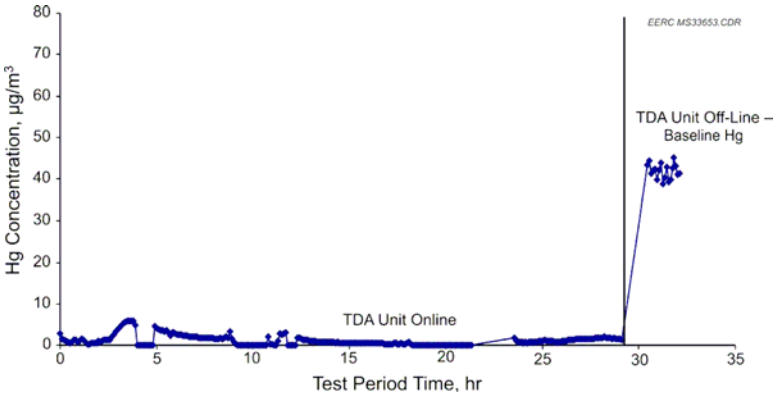

Figure 3. The Hg concentration at the exit of the TDA sorbent bed. T=210°C, P=100 psia, Hg Inlet = 40-50 μg/m^3 using coal-derived synthesis gas (UNDEERC data).

In the second test campaign at UNDEERC, we also showed the regeneration potential of the sorbent applying a mild temperature and pressure swing (by heating the bed about 25°C and reducing the system pressure to ambient). We used two sorbent beds to which we introduced synthesis gas for pre-determined durations. An automated valve system allowed us to direct the gas flow to each bed for desired durations. As part of the test plan, one of the beds, designated as Bed A in this report, was operated at 235°C and treated synthesis gas for a pre-determined duration or until the Hg breakthrough was observed from the bed, and then it was regenerated using clean synthesis gas recovered from the test skid by applying a mild temperature swing (20-30°C) at near ambient pressure. While Bed A was regenerating, the Bed B was on-line removing the contaminants from the synthesis gas. Provided that both of the sorbent beds were working properly, low concentrations of these contaminants were expected at the synthesis gas leaving our test skid at all times. TDA had a dedicated CEM to measure the Hg concentration from the regeneration bed, and another CEM to measure the Hg concentration in the synthesis gas leaving the test skid to confirm UNDEERC's measurements.

Altogether 5 absorption and regeneration cycles were performed with Bed A. Figure 4 shows the Hg concentration profiles as a function of time during regenerations for Cycle #1 and Cycle #3. The Hg capacity of the sorbent in the first cycle was far greater than the regenerated sorbent (this observation was in agreement with our bench-scale experiments at TDA facilities, where a decline in the Hg capacity of the sorbent was observed between the fresh sorbent –first cycle- and the sorbent capacity after a few cycles). We believe that by using a mild temperature swing it is not possible to drive all the Hg from the sorbent. However, the fact that sorbent achieved a high Hg removal efficiency following the regenerations suggests that the sorbent maintained a reasonable working capacity, and hence shows the technical feasibility of operating our sorbent in a regenerable manner under mild conditions to achieve a high sorbent utilization and thereby reducing the cost of mercury removal. As indicated by the data analysis

performed by UNDEERC, the Hg leakage from both sorbent beds was less than 5% throughout the test (except for Test 9 where TDA bed was put on-line only for a short time). This data shows that the TDA sorbent can operate in a regenerable manner, a particular advantage to

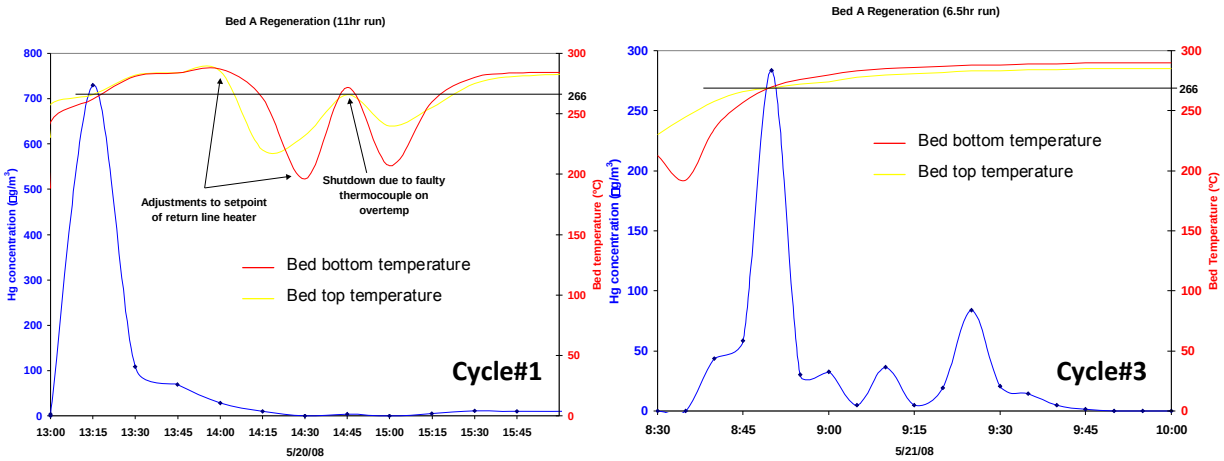

Figure 4. Hg concentration profiles during the regeneration of Bed A for Cycle#1 and Cycle #3 measured during the second gasification campaign at UNDEERC.

ensure cost effective operation at 260°C.

Following the tests, chemical analysis conducted on the spent sorbent samples recovered from different sections in the sorbent bed showed that modest amounts of other contaminants were accumulated in the sorbent bed. Figure 5 shows the mercury concentration measured for the sorbent samples removed from the inlet, middle and exit sections of the sorbent bed. As expected, the mercury levels were considerably higher in Bed B. Because Bed A was regenerated throughout the testing, the mercury accumulated in the bed removed periodically, no mercury accumulation was observed. Bed B was not regenerated so all of the mercury adsorbed throughout the five days of testing was present on the sorbent. Figure 6 shows arsenic and selenium accumulation over the inlet, middle and exit of the Bed A and Bed B. The analysis of the samples from these beds shows comparable amounts of contaminants accumulated in both beds, indicating that the conditions selected for the

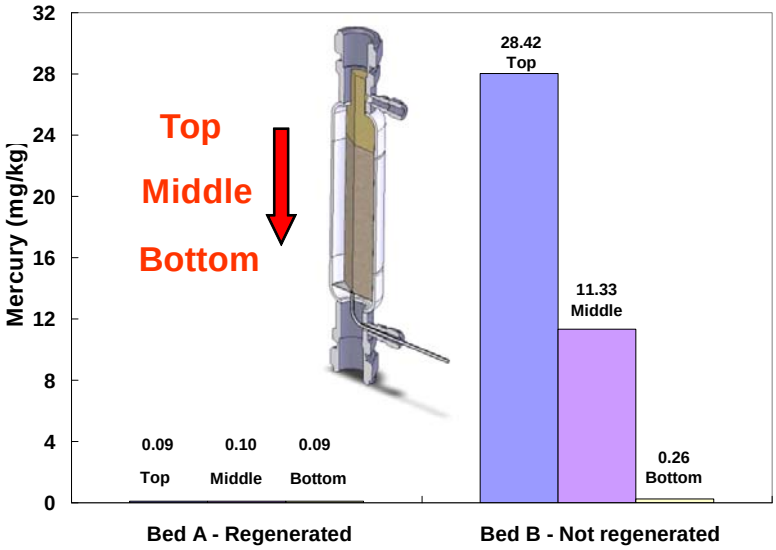

Figure 5. Chemical analysis results showing mercury accumulation at the inlet, middle and bottom section of the bed observed during the second gasification campaign at UNDEERC.

regeneration process is very mild and only removes mercury while irreversibly capturing all other contaminants during the regeneration. In our bench-scale experiments, we measured much higher capacity for our sorbent in arsenic and selenium removal. In the laboratory, in the absence of sulfur, we showed that the sorbent achieved up to 10% wt. capacity for arsenic (lb of arsenic per lb of sorbent) and selenium, while in the second test campaign at UNDEERC, we measured at most 0.014% wt. arsenic capacity (the sample taken from the inlet section of the bed). These results were somewhat expected, since we designed the sorbent beds for Hg removal (not for As, Se or Cd, because we knew from the bench-scale experiments that the sorbent has the lowest capacity for Hg). Because there was excess sorbent capacity for As and Se, we were not expecting the breakthrough of these contaminants from our sorbent beds. The cadmium levels in all sorbent samples were below the chemical analysis detection limit.

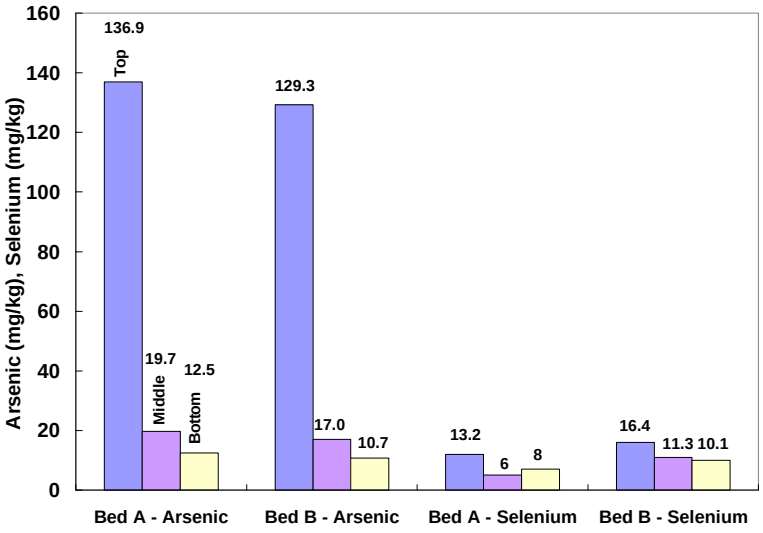

Figure 6. Chemical analysis results showing arsenic, selenium and cadmium accumulation at the inlet, middle and bottom section of the bed during 2nd gasification campaign at UNDEERC.

2.3 Summary of Contaminant Stability over the Used Sorbent Samples

At the end of the testing at UNDEERC, we recovered the tested sorbent sample and evaluated the stability of mercury subjecting the sorbent to an ASTM test (Synthetic Ground Water Leaching Procedure) designed to measure the leaching potential of the mercury from the sorbent following sorbent disposal. These tests showed that the mercury leaching will be negligible from the sorbent.

2.4 Summary of Cost Analysis

Finally, we included a preliminary economic analysis for our sorbent based trace metal removal technology. As part of the DOE Phase II SBIR project ("Sorbents for Mercury Removal from Coal Gasifier Effluents" Grant No. DE-FG03-02ER83551), TDA carried out a cost analysis for its trace metal removal system from coal-derived synthesis gas. As part of this project, we were planning to update this analysis using the sorbent capacity measured for the trace metal contaminants during the demonstration tests. However, because these field tests did not reveal any additional information on sorbent capacity (rather showed the technical feasibility of the concept and shed light to the fact that a very high Hg removal efficiency can be achieved at high temperatures for a number of synthesis gas streams generated by the gasification of different types of coal), we relied on the capacity data measured in our bench-scale experiments and retained the cost analysis results reported in the SBIR project. Based on major cost items, such as annualized capital cost, operating and maintenance expenses and sorbent replacement costs, we estimated that the cost of mercury removal as $2,995/lb. This analysis assumes that

the cost of removal of all other trace metal contaminants is included into this cost. At this cost, the incremental cost increase due to mercury control in an advanced gasification combined cycle power generation system is estimated as 0.23 mills/kWh, an increase of less than 1% over the cost of energy (which is assumed to be 35 mills/kWh). Thus, the effect of mercury removal on the cost of electricity using our high temperature cleaning process will be fairly small. We believe that the cost of the trace metal removal system will be dominated by the cost of removal of mercury due to the low capacity of the sorbents for mercury. Thus, the proposed costs will also cover the cost of removal of all other trace metal contaminants.

2.5 Conclusions

As part of the test program, we carried out four demonstrations at two different sites using the synthesis gas generated by the gasification of various lignites and a bituminous coal. Two of these tests were conducted at the Power Systems Demonstration Facility (PSDF) in Wilsonville, Alabama; a Falkirk (North Dakota) lignite and a high sodium lignite (the PSDF operator Southern Company did not disclose the source of this lignite) were used as the feedstock. In collaboration with the University of North Dakota Energy Environmental Research Center (UNDEERC), we also carried out two more demonstrations using synthesis gas slipstreams generated by the gasification of Sufco (Utah) bituminous coal and an Oak Hills (Texas) lignite.

Overall, the test results indicate that the TDA sorbent is capable of removing multi-contaminants in the coal-derived synthesis gas at high temperature. TDA sorbent successfully removes Hg from the synthesis gas streams generated by different gasifiers using different coals at different sites and achieve greater than 95% Hg removal efficiency at 260^{o}C. This sorbent can be operated in a regenerable manner to remove Hg from the bed, while irreversibly removing all other trace metals including As, Se and Cd with high capacity.

The fate of mercury has been evaluated in a Synthetic Ground Water Leaching Procedure Test, and has been shown that it will remain on the sorbent once the sorbent is disposed.

Based on a preliminary engineering and cost analysis, TDA estimated that the cost of mercury removal from coal-derived synthesis gas as $2,995/lb. This analysis assumes that the cost of removal of all other trace metal contaminants is included into this cost. The projected cost will result in an increase of less than 1% over the cost of energy.

2.6 Recommendations

The DOE project provided enormous insight to develop an understanding and knowledge base on our novel trace metal removal sorbent and gas clean-up process and confirm its performance capabilities while treating actual coal-derived synthesis gas. The synthesis gas generated at the test sites were highly representative of actual gasification processes that enabled evaluation of the sorbent under highly relevant conditions.

A major problem observed during the demonstration tests was related to the limited duration and intermittent operation of the pilot-scale gasifiers (because it is expensive to operate them for long durations). It is recommended that the performance of the Test Skid be evaluated for longer durations to gather more information on the breakthrough of the metal contaminants in addition to mercury. Longer test durations will also allow us to demonstrate the regeneration capability of the sorbent for a higher number of cycles (in the current tests, we were able to demonstrate 5 absorption/regenerations).

The commercial TDA design involves the use of semi moving-bed reactors to house the sorbent. By always providing a fresh batch of sorbent at the reactor exit, the moving-bed reactors ensures high removal efficiency of the contaminants. The spent sorbent removed from the reactor has the longest exposure to the contaminants at high concentration, which increases its utilization. Thus, it is recommended to demonstrate the sorbent performance in a semi moving-bed reactor.

Finally, a detailed cost analysis must be carried out to fully assess the benefits of the new technology. The preliminary cost analysis carried out in this and earlier projects were highly limited in scope. A detailed and preferably an independent cost analysis must be carried out to evaluate the economic impact of the new technology.

3. Results

3.1 Construction of the Test Skid

Early in the project, TDA designed and built a skid-mounted prototype system capable of being moved to a test site, and fully testing our novel sorbent and high temperature trace contaminant removal process. The prototype test skid contains three sorbent reactors that are capable of evaluating sorbent performance at different operating conditions.

Figure 7. Prototype remote testing system.

Figure 7 is a photograph of the skid-mounted system, which was originally sized to treat 10,000 SCFH of coal-derived synthesis gas. This selected capacity represents a 250-fold increase from the bench-scale system. The prototype unit was sized so that the results could be directly scalable to the higher gas flow conditions encountered in full-size installations. The key features of the test skid include the following:

1. Three high temperature reactors that could be operated independently from one to another to demonstrate the efficacy of the sorbent in removing trace metal contaminants at a range of operating conditions
2. Flow selection valves with automated actuators that switch reactors between absorption and regeneration modes, and appropriate gas manifolding
3. All auxiliary components to be able to regenerate the sorbent (as desired)
4. Appropriate pressure control system
5. Appropriate heating and cooling systems
6. A fully automated data control system to control, monitor and log all operating parameters
7. An analyzer rack that includes various on-line analyzers with gas sampling and conditioning capabilities

The test skid was designed for on-site, stand-alone, unattended testing of TDA's heavy metals removal sorbent at coal gasification facilities. The design incorporates three beds for flexibility in unattended testing. The unit interfaces consist of inlet and outlet points for synthesis gas, connections for facility power, compressed air hookup for the pneumatic systems, and a computer connection for control and data collection. All piping, reactors and valves exposed to synthesis gas are constructed of 316 stainless steel with connections by Swagelok compression fittings or welds. Valve seats and seals were selected for compatibility with synthesis gas and contaminants at the temperatures and pressures expected during operation. As such, the primary flow control valves are 1" Swagelok steam service valves with PEEK seats and grafoil seals, with a maximum service rating of 1100 psig at 287ºC. These all include pneumatic actuators for automated flow path control by the system. Additionally, in the event of a failure or safety shutdown, the valves all close (either by the control programming or air-to-open

actuators) to isolate the reactors. All components were selected and designed for operation at condition of at least 250 psi at 260˚C. All auxiliary components required for the operation of the prototype unit are shown in the process and instrumentation diagram (P&ID) in Figure 8.

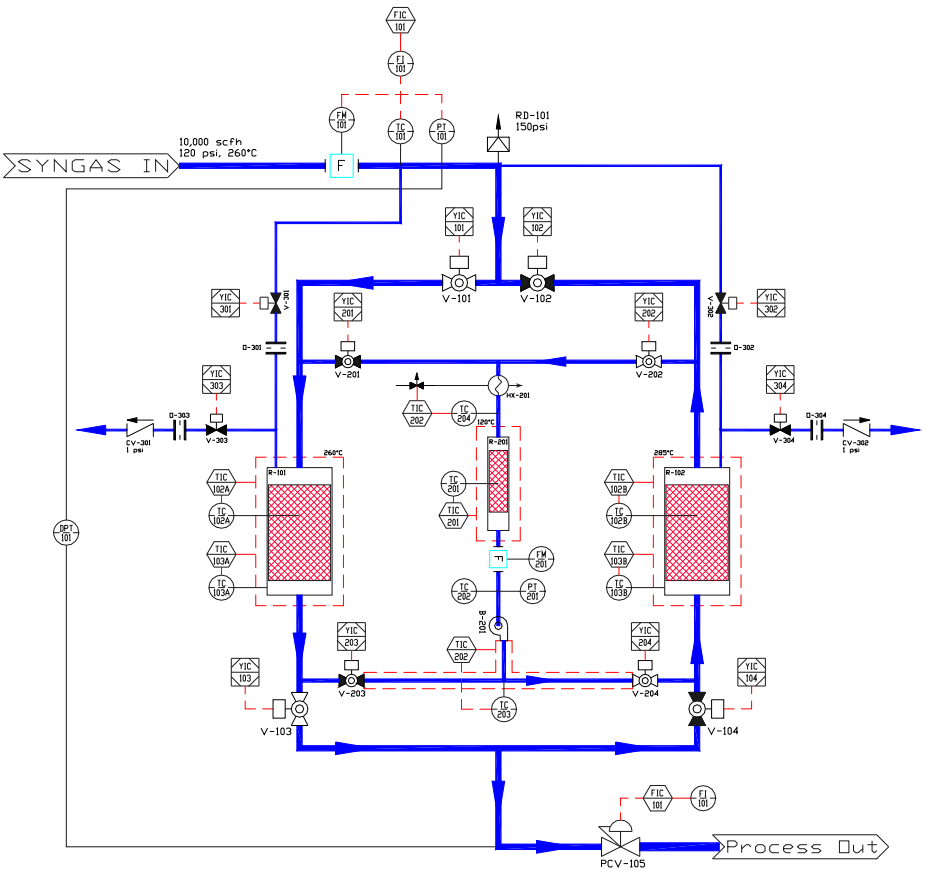

Figure 8. P&ID of the TDA's prototype system.

The system was designed to operate on a slip stream or the whole output of a laboratory-scale gasifer (such as UNDEERC's) with the exhaust gas sent to a low-pressure vent, a thermal oxidizer, or a recovery system. Flow rate control in slip stream operation is accomplished with the use of a Badger process control valve and pitot probe flow meter. The process control valve uses a positioner and a variable orifice, with the positioner output fed by a P&ID control loop in the system reading the pitot probe flow. System pressure is set by the delivery pressure from the gasifier.

The control system had several features that continuously monitored all critical operating parameters. In the event of any unexpected deviations from the desired range, a shut down sequence was activated to safely and promptly terminate the testing. Safety shutdowns are accomplished by a control system monitor, but there were also mechanical backup monitors and shutdowns in place in case of a malfunction of the control system. These include over temperature modules for all heaters and a combustible monitor in the unit. In case of any leaks in the system, based on the monitor's response the system will automatically shutdown. TDA completed the first draft of a "Safe Operating Procedure" for the unit, covering basic safety issues and control points for the safety monitor. Prior to any demonstrations, TDA held

meetings with the plant operators and site representatives to qualify the test skid for operation at a particular site. The operation procedures of the test skid and the safety features were adjusted based on the requests of the demonstration facility.

Tubing: Tubing for the system was specified to be 1" x 0.083" wall Stainless Steel. Based on the tubing data in the Swagelok catalog, the working pressure rating of this tubing, assuming 304 SS seamless drawn tubing is 3100 psi. If using single-welded tubing, this pressure is de-rated by a factor of 0.8 for a new working pressure of 2480 psi. Since the system will be operating at 260˚C, an additional de-rating factor must be used. For operation at 315˚C, the de-rating factor for 304 SS is 0.82. This gives a final working pressure of 2033.6 psi. These ratings are based on Swagelok tubing data, referencing ASTM A269 and ASME B31.3. We multiplied stainless steel rating by 0.94 for working pressure in accordance with ASME B31.1. This additional de-rating factor results in a working pressure of 1911.58 psi, well over the system operating pressure.

Fittings: The fittings used on the system were Swagelok brand tube fittings. Swagelok tube fitting ends are rated to the working pressure of tubing as listed in the Swagelok tubing data catalog. Pressure ratings for fittings that have both tube fitting and pipe thread ends are determined by the end connection with the lowest pressure rating. For a 1" female NPT fitting, the room temperature pressure rating is 4400 psi. At elevated temperature its pressure rating drops to 3608 psi. This fitting is capable of withstanding higher pressure than the tubing used in the system.

System Control Valves: The valves used to direct flow within the system are 1" Swagelok steam service ball valves. These valves have a working pressure of 1100 psi at 287˚C.

Control Valves: At the exit of the system, a Badger Research Control Valve was used to control the flow through the system. The Badger valve was rated to operate at 1050 psi at 315˚C.

Sorbent Bed: The sorbent bed was designed to operate at up to 250 psi at 285˚C. The original design utilized 6" sch 10 pipe. Welding an end cap to the pipe formed the bottom end, while the top was made to be accessible by constructing it from flange fittings. This design allows easy access to fill the sorbent and extract it for testing after completing operational tests on the unit. However, the flange fittings are large, heavy and difficult to heat and insulate adequately. The "low-pressure" design required class 300 flanges that were over a foot in diameter and nearly 1 ½" thick. The pair of mating flanges for each reactor weighs approximately 90 lbs.

Reactors (original design): The original design called for a process flow rate of 10,000 SCFH for treatment. Thus, the first generation sorbent vessels were designed to handle this gas volume. The original reactors have a 6.0" OD (5.98" ID) and 20.7" length (Figure 9). The internal volume of these reactors will be 581 in^3, about 85% of this volume will be occupied by the sorbent. To reduce cost, the vessels will be made from 6" schedule 10 pipe and fittings, along with class 300 flanges for the top section. The bottom of the reactor will be welded cap. The total weight of each reactor is estimated to be around 100 lb (including about 8lbs of sorbent).

The reactors use an inert insert to house the sorbent, which allowed us to remove the sorbent easily at the end of the test and extract sorbent samples to be sent for chemical analysis (Figure 10). This was needed to observe the accumulation of the trace metals across the bed and assess the absorption capacity of the sorbent for the metals other than mercury. The reactor was rated to 250 psig. The gasification system at UNDEERC is capable of delivering a synthesis gas stream at 120 psig. We designed all system components rated to higher pressures, thus eliminating any hazards related to over pressurization of the system. The higher pressure rating of the system also enabled the use of our test skid at different facilities that could deliver synthesis gas at higher pressures (such as the PSDF that could deliver synthesis gas at 250 psig).

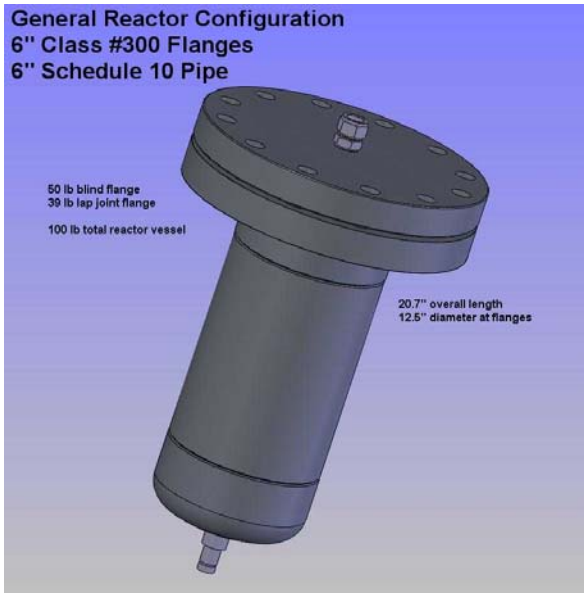

Figure 9. The specifications of sorbent reactor.

Control System: The system is controlled automatically by an Opto 22 control system. All the PID modules that allow us to monitor and to control the critical operating parameters (e.g., temperature, pressure, contaminant concentration) were installed into a box as shown in Figure 11. The control system is automated and designed to run experimentation unattended. All heater control points, flow control valving, and flow rate control can be altered by the system. To facilitate extended operation, a third bed was installed to permit contaminants to be removed from the primary beds once they reached saturation. Consequently, the system was also designed to permit and control this gas-phase transfer to the third bed. The programming allows for up thirty test conditions to be run unattended, with cyclic testing of both primary beds.

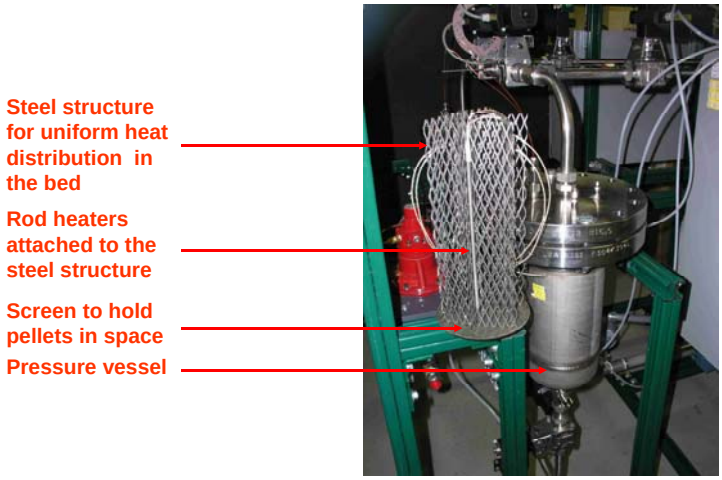

Figure 10. The sorbent reactor and the insert.

Extensive safety interlocks are programmed into the control system to facilitate safe unattended operation. Every pressure and temperature data point is monitored continuously against an appropriate maximum based on the location within the system and associated equipment at that point.

Valve positions are monitored versus pressure, and additional interlocks prevent against operating the valves across a high differential pressure. This prevents low pressure components from being exposed to high pressure, but also prevents pressure waves from damaging the system, the sorbent, or upstream components. It also reduces pressure waves

and flow variability in upstream systems that may be easily upset, including the gasifier itself. Reactor pressure changes are gradual, and controlled by a separate system of orifices and valves under system control. The system continues testing on one bed if a non-critical failure disables the other bed. Non-critical failures are those that affect normal system operation without creating an unsafe condition for personnel, the system, or facilities.

Figure 11. Primary control box for the system.

As the control system can vary the flow path as well as the flow rate, the control programming was designed to step through multiple test parameters without operator intervention. Up to thirty steps can be entered, with any step corresponding to any one of thirty-two parameter conditions. Each set of parameter conditions includes set points for primary gas flow path, secondary gas flow path, and primary flow rate, as well as set points for every heater in the system and step time. Figure 12 shows the screenshot of the user interface.

Modified Reactors: While the initial reactor design was for a synthesis gas feed rate of 10,000 SCFH, testing at PSDF and UNDEERC was going to be done at much lower rates. Both facilities were set up for synthesis gas delivery of 300 to 500 SCFH,

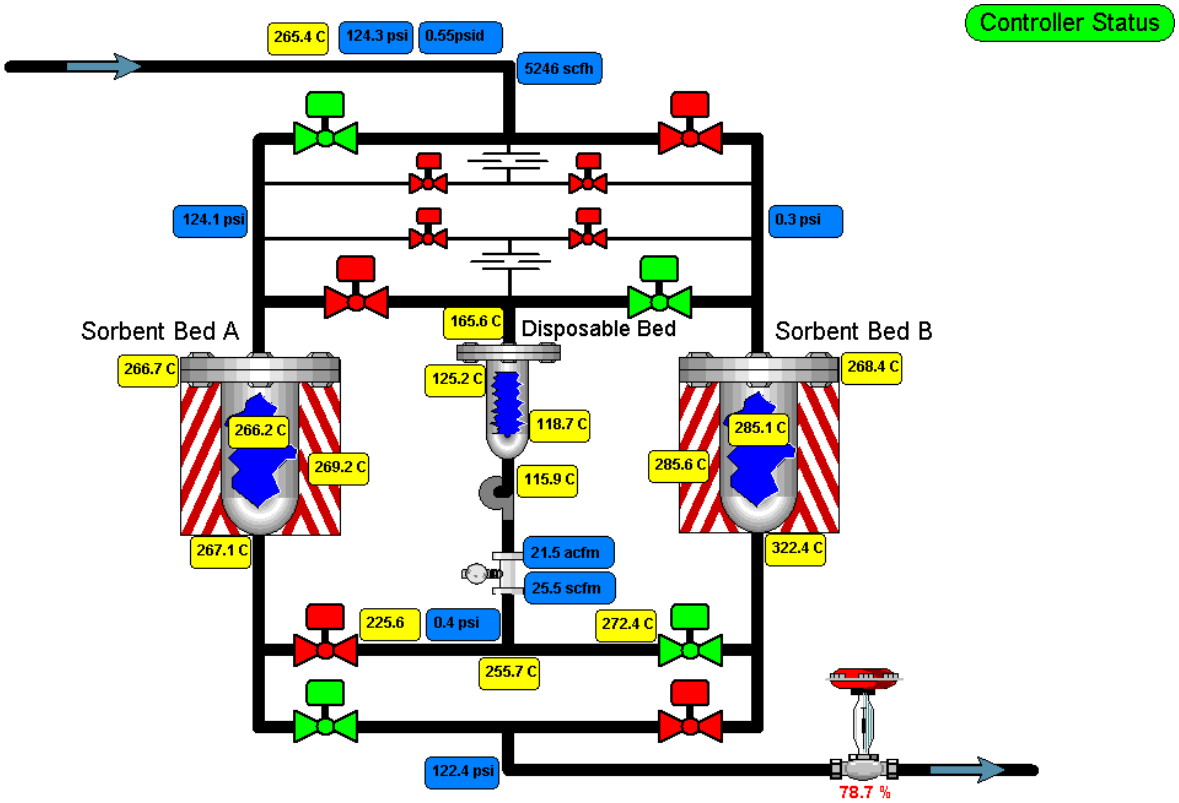

Figure 12. Screenshot of the user interface.

significantly lower than the original reactor design. In order to observe breakthrough of the trace contaminants within the 2 weeks test period at the lower gas flows, TDA decided to reduce the size of the high temperature sorbent reactors from 5.7L of sorbent per bed to 600mL of sorbent per bed. Although the gas flow was reduced by a factor of 20, the bed size was not reduced at the same proportion to accommodate the higher arsenic and selenium content of the low grade lignite that will be used in the gasification tests, versus that of PRB coal that the original reactors were designed to test.

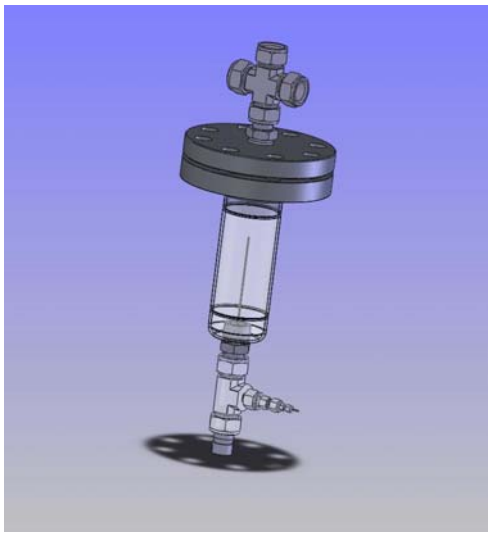

Figure 13. Schematic of the reactor used in the first PSDF campaign.

These reactors retained the flanged design and total length of the previous reactors, with a smaller pipe size and shorter reactor length to reduce the bed volume. Fittings were added to the top and bottom of each reactor to maintain the total length and provide access points for additional internal temperature measurements. The first test campaign at PSDF utilized the 600mL reactors, shown in Figure 13 and Figure 14, while the rest of the system remained as originally designed. These reactors are 2.5" Sch 10 304L SS Pipe, rated to 818psi working pressure at 315°C. We used Class 300 flanged end, rated to 360 psi working pressure @ 315°C. As it was in the earlier design, we used a lap joint flange, which could be rotated to align fittings in top flange during assembly. The lap joint configuration also creates thermal break to reduce heat loss from vessel to flange.

Figure 14. Picture of the initial PSDF reactor.

Additionally, the pitot probe flow meter was sized for pressure drop expected by a 10,000 SCFH synthesis gas feed and could not be scaled to the 500 SCFH maximum expected at the PSDF test facility. The pitot probe was left in place, but the flow measurement was accomplished by a turbine flow meter placed at the outlet of the system. By placing it downstream of the flow control valve, the turbine flow meter is measuring flow at the lowest pressure point in the system

for the highest volumetric flow and best flow signal. Internal PID control loops were modified to use the turbine input instead of the pitot probe.

This sorbent volume was still too large to achieve metals saturation at the test flow rate during the first campaign at PSDF, so the reactors were redesigned again to a 250mL sorbent volume with a simple welded pipe design. The sorbent was activated in the reactors at TDA, then sealed and shipped to PSDF for installation into the system. The intermediate reactors were removed and shipped back to TDA with the sorbent still sealed inside. Orifice sizing was altered during this campaign to reduce the depressurization rate of the beds. These reactors and orifice sizing were retained for testing at UNDEERC.

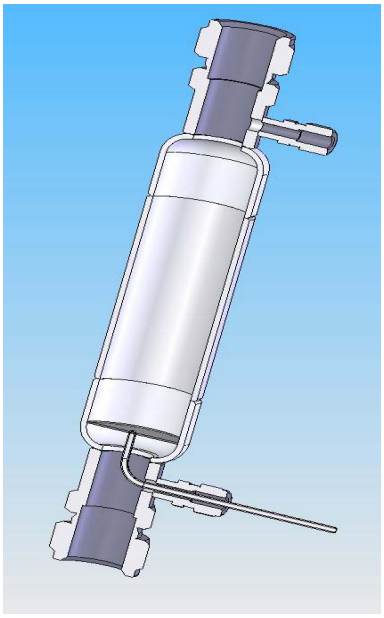

Figure 15. The schematic of the reactor designed used at the gasification campaigns at UNDEERC.

Testing at UNDEERC brought about another round of modifications to the system to interface with their gasifiers. The facilities at UNDEERC were arranged to allow the synthesis gas to be used for other testing downstream of the TDA Trace Contaminant Control System. As such, the outlet pressure and flow control were set by downstream external components. The system outlet was modified to feed downstream components directly without the use of the control valve, which would have caused excessive pressure drop. The control valve was then plumbed to open a system bypass line in the event of a shutdown, minimizing disruption to the upstream and downstream components.

3.2 Demonstration Tests at PSDF

The objective of this work was to demonstrate the potential of TDA's Multi-contaminant Clean-up System using actual coal-derived synthesis gas. For the demonstration, we were to collaborate with the University of North Dakota Energy Environmental Research Center (UNDEERC). As written in the proposal, TDA would not have to pay for the cost of operating the gasifier, but only the labor needed to supply a slipstream of the synthesis gas to TDA test skid, and all the labor and supervisory support for installing the test skid at the site, as well as to carry out an independent measurement of mercury concentration. Thus, the TDA demonstration tests were piggy-backed on another project, where one of UNDEERC's commercial clients would have paid for the operation of the gasifier (the major cost). However, due to lack of funding at the UNDEERC, the demonstration test had to be postponed several times. Based on the suggestion of the DOE Project Manager, TDA made new arrangements to carry out the test at the Power Systems Demonstration Facility (PSDF) in Wilsonville, Alabama.

As part of our work at the PSDF, TDA carried out two demonstration tests using a slipstream of coal-derived synthesis gas provided from the Transport Gasifier (in fact TDA personnel were present on three different occasions at the PSDF, however, in one of these tests our test skid never received any gas because the gasifier could not be operated at steady-state and the testing had to be terminated). Our objective was to develop an understanding and knowledge base on our novel trace metal removal sorbent and gas clean-up process while treating actual coal-derived synthesis gas. For these tests, two different types of coals were selected as the feedstock. In the first test, a Falkirk lignite was fed to the gasifier. In the second test, the Southern Company did not disclose us the source or the composition of the coal; the coal used in the second test campaign is referred to as "high sodium lignite" in our report. These tests were conducted as part of a different lignite gasification project undertaken by the Southern Company. TDA tests were again piggy-backed on the testing being conducted at the PSDF and neither TDA (nor the DOE project) paid for the operation of the gasifier itself.

Although our test skid was designed for the demonstration at UNDEERC, we had designed and fabricated a highly versatile system that could be integrated into various gasification facilities with only minor modifications in the system. For instance, we designed all the piping and manifolds for a much higher pressure and temperature rating than we would have experienced at UNDEERC. By replacing a small number of components, we were able to qualify the system for the PSDF tests. Our skid was designed for American Society of Mechanical Engineers (ASME) pressure piping codes. However, because the electrical heaters or instrumentation were not rated to Division II Group B, TDA located all electric heaters and spark sources under a vented enclosure (having positive pressure within that area all the time preventing any leakage of combustible gases that could potentially cause a hazard).

TDA provided a stand-alone data acquisition system to measure operating parameters within the TDA test skid. All other data related to synthesis gas composition, temperature, pressure and contaminant concentration (Cl, S etc.) were monitored and logged by the Southern Company. Southern also provided the staffing required to operate the gasifier and auxiliaries (such as the sulfur reactor). Unfortunately, the PSDF did not have any on-line measurement capability for the trace metal contaminants during the time of the testing, and they did not provide any gas sampling and analysis related to the concentration of target trace metal contaminants. To be able to carry out measurements, TDA provided two separate Hg analyzers for on-line Hg measurements and an arsine analyzer was also used to measure sorbent's efficacy in removing arsenic. Our plan was to rely on post-run analysis of the sorbent samples

taken from at different locations in the sorbent bed to assess the performance of the sorbent in removing all other trace metal concentrations (e.g., selenium, cadmium).

It was Southern Company's objective to evaluate the suitability of some of the low cost (also low quality) lignites in their gasifiers. The gasification campaign at PSDF was originally scheduled to last for 3 weeks. A low grade, high sodium Falkirk lignite was selected as the feed to the plant. Through the course of three separate gasification campaigns in November 2006, January 2007 and March 2007, it was found difficult to feed the selected lignite coals to the gasifier, causing unscheduled gasifier shutdowns due to problems encountered in the coal feeder. Appendix B provides details of the PSDF.

3.2.1 Test Plan

Because Southern's experience with these coals was fairly limited, the information related to the synthesis gas composition and related contaminant concentration was also limited. In preparation for these tests, TDA had to make a highly conservative decision for the selection of the sorbent bed size, designing the beds for a 12-day (288 hr) operation assuming 35 $\mu g/m^3$ Hg in the synthesis gas (this assumption was based on the Hg concentration present in the coal by the elemental analysis carried out by the Southern Company).

It was our objective to identify the breakthrough capacity of the sorbent at least for mercury. Due to the low sorbent capacity for Hg, we expected that during the test duration we could observe the mercury breakthrough from the bed. Based on the bench-scale experimental results conducted at TDA, we were expecting a relatively higher capacity for all other trace metal contaminants. Hence, our objective was to confirm the absence of slippage of these other trace metal compounds from our bed, and to rely on post-experiment chemical analysis on the sorbent bed to measure the capacity of the sorbent for these other contaminants.

In these tests, we also had plans to evaluate the potential for regenerating the sorbent. Our test skid contained three separate sorbent beds and appropriate valves to direct the synthesis gas flow through each of the beds (one bed can be on-line at a given time). As part of the test plan, one of the beds, designated as Bed A in this report, was to treat synthesis gas for a pre-determined duration or until the Hg breakthrough was observed from the bed. The bed would then be regenerated using clean synthesis gas and applying a mild temperature swing (20-30^oC) at near ambient pressure. While the Bed A was regenerating, Bed B will be on-line removing the contaminants from the synthesis gas. Provided that both of the sorbent beds were working properly, a low concentration of these contaminants was expected in the synthesis gas leaving our test skid at all times. TDA had a Hg analyzer and an arsine analyzer to measure the concentration of the contaminants leaving the test skid. An additional Hg analyzer was in place to evaluate the Hg concentration released from the regeneration bed.

In both demonstrations, our plan was to maintain both Bed A and Bed B at 260^oC to demonstrate the high temperature contaminant removal capability. In both test campaigns, we were supplied with a small fraction of the synthesis gas produced by the Transport Gasifier. A hot gas particulate control system removed the dust, ash and unburned coal from the gas. For the gasification campaign at PSDF, there were already two other demonstrations in place; evaluation of an activated alumina type commercial COS hydrolysis catalyst (converting COS to H_2S for easy removal) and a ZnO-based commercial desulfurization sorbent to remove the H_2S. Southern Company did not disclose the product number, producers or any other information

related to the chemical composition of these materials. The TDA system was located downstream of these two reactors.

As mentioned previously, TDA's trace metal removal sorbent showed high sensitivity to sulfur. Ideally, our test skid should be located downstream of a bulk desulfurization system. We realized that warm gas desulfurization systems still generate a synthesis gas that is contaminated with 1 to 5 ppmv or in some cases even higher concentrations of sulfur. At these low sulfur concentrations, our sorbent removes the trace contaminants while also polishing for sulfur removal, reducing the sulfur concentration to ppb levels and providing deep desulfurization of the synthesis gas. However, if the sulfur concentration of the synthesis gas is too high, then an undesired sulfide phase forms, rendering the sorbent inactive for trace metal removal. Thus, TDA skid was located downstream of the commercial ZnO bed, receiving a low sulfur synthesis gas. The synthesis gas flow to our test skid ranged from 400 to 500 SCFH.

3.2.2 Qualification for Test Site

TDA and Southern went through several evaluations to ensure safe operation of the test unit and meet Southern Company's requirements for the PSDF test site. First, we generated a utility requirement list based on the needs of the test system while conducting the experiments (Figure 16). Southern Company agreed to make minor modifications at the test site mostly to accommodate the electrical needs of the system. TDA and Southern also conducted a detailed

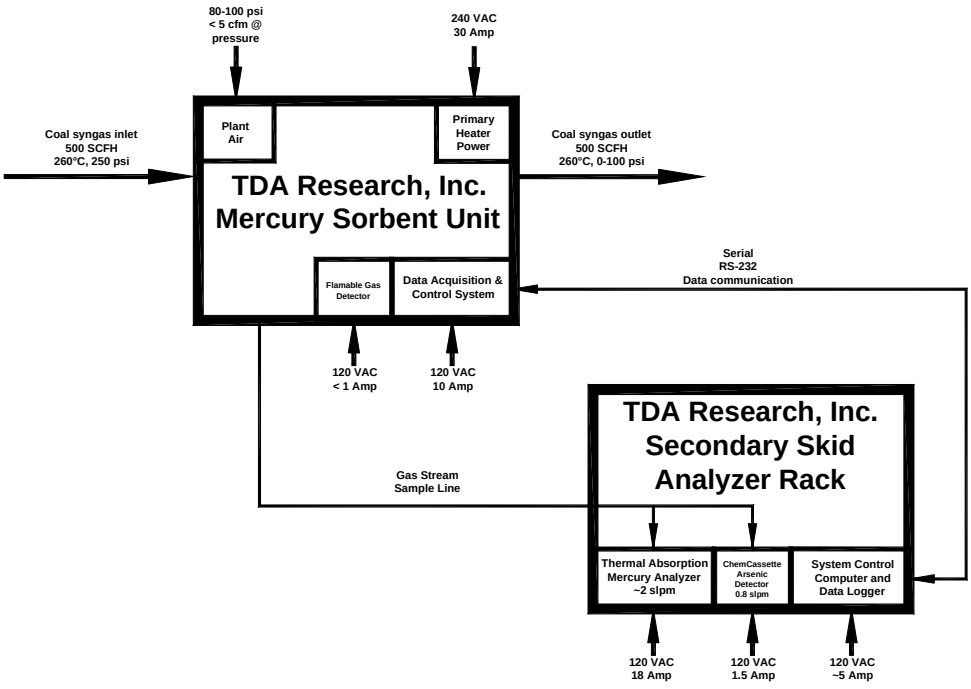

Figure 16. Utility needs for TDA's Test Skid and Analyzer rack.

"Design Hazard Review", which qualified our prototype for testing at the PSDF. In addition to providing process instrumentation diagrams (PIDs) and equipment specification charts, TDA completed a "Safe Operating Procedure" for the unit, and provided detailed information on the experimental plan, start-up and shutdown sequences. The few minor modifications requested by Southern were incorporated into the test skid (e.g., a relief valve in the circulation loop, a control loop at the gas exit line that senses any over-pressurization in the gas exhaust to initiate shutdown). TDA and Southern Company also signed a "Site Access Agreement". The agreement required TDA to provide liability coverage up to $3 million at the test site. TDA paid the cost of insurance at no-cost to the project as part of the cost share to the project.

3.2.3 PSDF Test Campaign #1

Coal Properties: The proximate–ultimate, x-ray fluorescence (XRF) ash, and heating value analyses for the Falkirk lignite are shown in Table 3.

Table 3. Specifications of the Falkirk lignite used in the first demonstration tests at PSDF.

Falkirk lignite	
Ultimate Analysis, wt%	
Hydrogen	4.5%
Carbon	59.0%
Nitrogen	8.9%
Sulfur	1.1%
Ash	17.0%
XRF Ash Analysis, wt%	
SiO2	40.0%
Al2O3	11.0%
Fe2O3	6.1%
TiO2	0.5%
P2O5	0.2%
CaO	11.0%
MgO	3.0%
Na2O	8.4%
K2O	1.4%
SO3	15.0%
Heating value, Btu/lb	9600
Trace Metals Analysis, μg/g	
Arsenic	7.6
Cadmium	0.079
Mercury	0.15
Selenium	0.8

In the Test Campaign #1, the two sorbent beds in the trace-contaminant control system were intermittently tested over the course of 9 days. In the evaluation, the sorbent beds were first brought up to the operating temperature (260°C) under the flow of low pressure nitrogen. Nitrogen was introduced to the system through heat-traced lines, which were also used to provide the synthesis gas slipstream to the test system. The nitrogen flow rate was adjusted to 400 SCFH to ensure little or no variation of the operating parameters when switched to synthesis gas. Additional external heaters and heavy insulation around the sorbent reactors provided the heating to maintain the gas temperature at 260°C. Several measurements at the inlet and the exit of the bed (as well as within the bed) confirmed a uniform temperature distribution. Once a stable bed temperature was maintained, the bed pressure was increased to 200 psig operating pressure using high pressure nitrogen. After the pressure and temperature were stabilized at the desired set points, the synthesis gas was introduced to the first sorbent bed (Bed A).

Figure 17 summarizes the 9-day test profile. The gasification campaign started on 11/13/06. Once the gasifier operation was stable, the testing on the TDA skid started the next day. We first introduced low pressure nitrogen into the skid during the heating of the bed to the desired operating temperature. This is followed by flowing high pressure nitrogen to pressurize both beds to the desired operating pressure. Once stable temperature and pressure was maintained in the beds, the synthesis gas was introduced first to Bed A on 11/15/06. Bed A was on-line for 24 hrs before the gasifier was shutdown due to problems in the coal feeder. We switched to high pressure nitrogen in the absence of synthesis gas to maintain system temperature and pressure. When the gasifier was fixed and back in operation, the synthesis gas was re-introduced into Bed A, however, due to an errant reading TDA's system shutdown. We restarted the system again and synthesis gas was introduced to Bed A. On 11/21 we switched the gas flow to Bed B, which was on-line for about

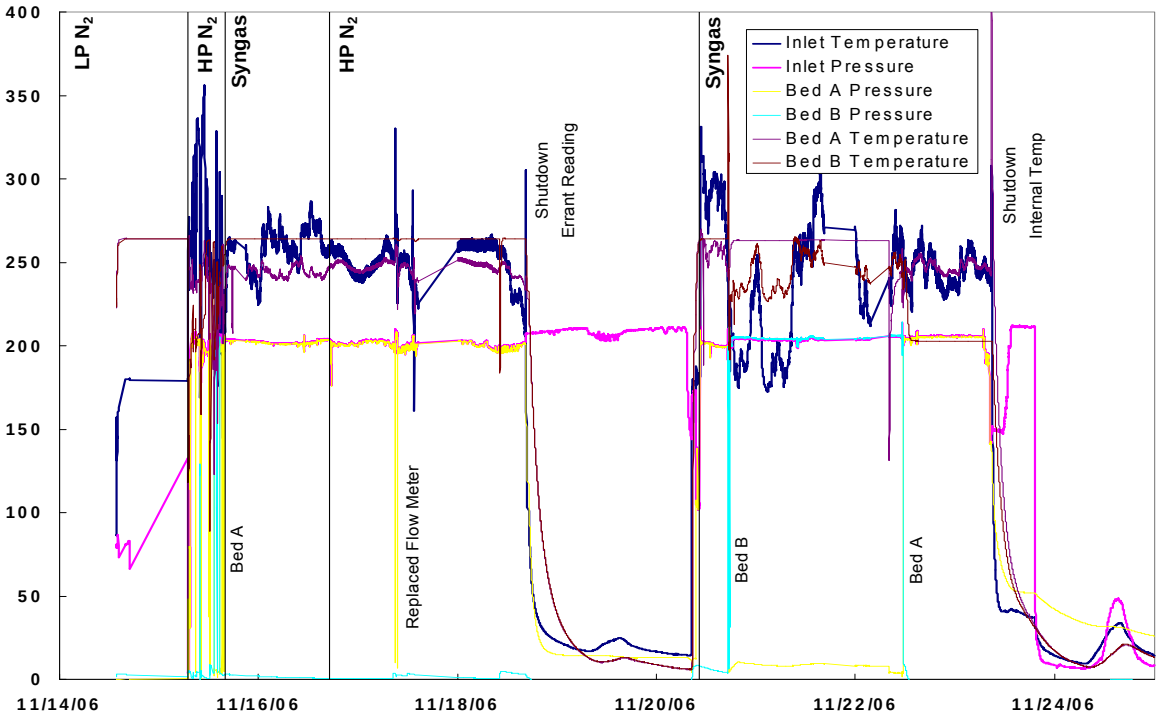

Figure 17. Temperature and pressure profiles in the test beds during the first campaign at the PSDF.

24 hrs. During this time, we regenerated Bed A to observe the presence of any mercury release by mild temperature swing. However, because of a malfunction in the Hg analyzer located in the regeneration loop, no useful data were collected. With the assumption that the regeneration was complete, Bed A was put back on-line. After a short time the beds switched, the gasifier again shutdown, and eventually the test was terminated.

In each bed, we loaded 480 g of sorbent in the form of 1/8" cylindrical pellets. The sorbent beds were sized based on 35,000 ng/m^3 Hg concentration in the synthesis gas (based on the coal characterization and the dilution in the gasification process) and for 7 days (168 hrs) of continuous operation in each bed to support a total of 2 week continuous demonstration test. However, due to the gasifier shutdowns, the actual test duration was only 4 days (96hrs), with Bed A and Bed B treating 3,022 lb (40,940 SCF) and 1,035 lb (14,020 SCF) of synthesis gas, respectively.

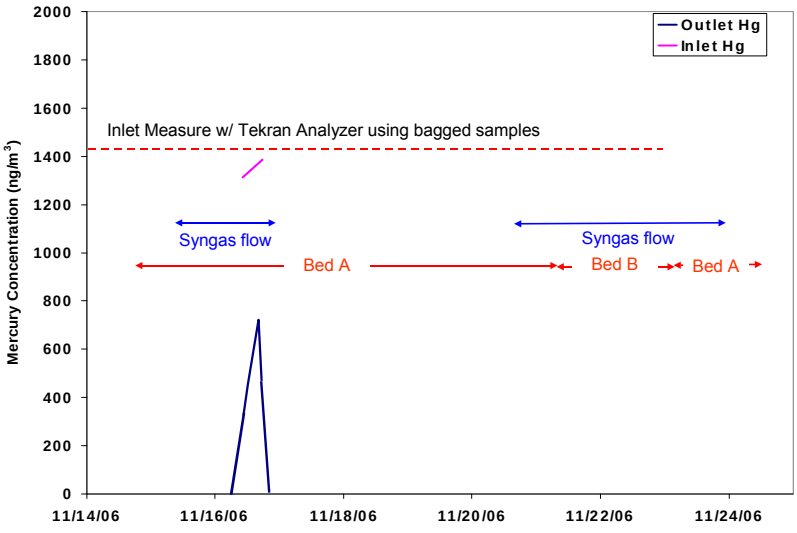

Figure 18. Hg concentration profiles at the inlet and exit of the bed.

Figure 18 shows the Hg concentration profiles at the inlet and exit of the system.

We measured the mercury concentration of the inlet gas using an Ohio Lumex Analyzer (Figure 19), showing that the synthesis gas slipstream supplied to the test system contains about 1,400 ng/m^3 of Hg. Hg concentrations at the exit of both beds were below the detection limit of the analyzer, with the exception of a short duration immediately after which an inlet sample was taken. Because we used the same gas lines and manifolds for sampling from the inlet and the exit of the system, the Hg concentration measured for the short duration at the Bed A exit (during 11/17/06 timeframe shown in Figure 18 is attributed to the leftover Hg remaining in the samples lines).

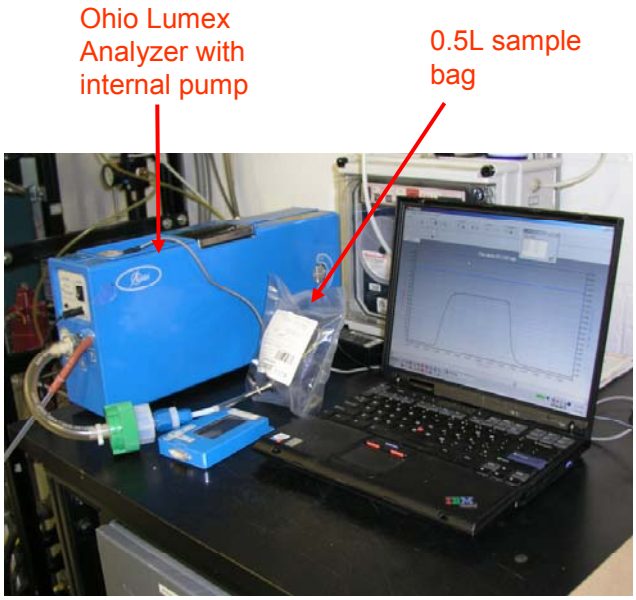

Figure 19. Gas sampling bags and the portable Ohio Lumex Hg analyzer.

The portable field analyzer selected to measure the Hg concentration during the demonstration tests had a detection limit of 100 ng/m^3. Because the Hg concentration of the gas was much lower than expected, to provide an independent confirmation to ensure that a very high Hg removal efficiency is indeed accomplished, we also collected gas samples both at the inlet and exit of the system using Tedlar bags which were shipped back to TDA for a more thorough analysis (both to confirm that the Hg concentration at the inlet was as low as indicated by the portable Ohio Lumex analyzer (Figure 19) and independently validate the sorbent performance). At TDA we used a Tekran 3300 CEM to analyze the Hg content of the bagged samples (Figure 20). The Tekran CEM has Hg speciation capability, enabling detection of not only the elemental Hg, but also the oxidized forms of Hg such as $HgCl_2$ and HgS. The analysis results with the Tekran CEM were in agreement with the portable field analyzer, showing that the Hg content of the synthesis gas was about 1,425 ng/m^3 and all mercury was present in the elemental form.

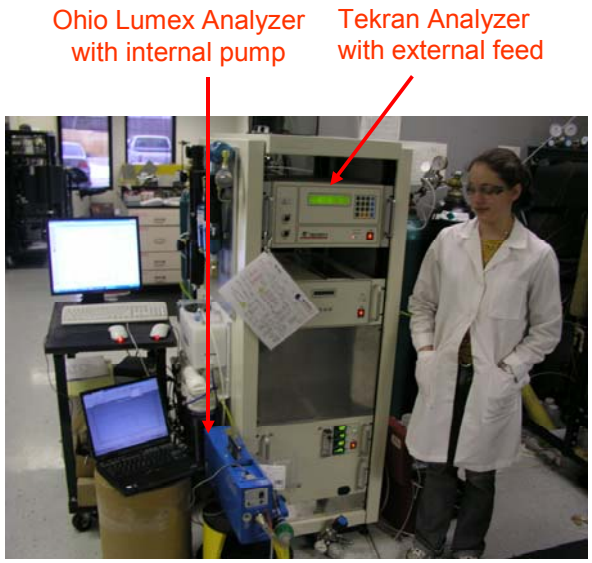

Figure 20. Tekran 3300 CEM and the portable Ohio Lumex analyzer.

Although the sorbent successfully removed Hg at high temperature (260^{o}C) and achieved near 100% removal efficiency, we could not draw any meaningful conclusions on its capacity because the sorbent bed was significantly oversized for the test conditions (e.g., the test duration was much shorter than planned and the Hg concentration was much lower than anticipated).

During these tests, we could not show the arsenic removal performance of the sorbent because the analytical system did not detect any arsine (AsH_3) at the inlet or the exit (10 ppbv detection limit). One may speculate that the arsenic was retained in the upstream ZnO desulfurizer or the COS hydrolysis catalyst bed, although both the ZnO and the activated alumina based COS hydrolysis catalyst were known to be relatively inert for arsenic removal (arsenic usually interacts with the metals rather than these oxides). In fact, TDA carried out gas analysis after the COS hydrolysis bed (before the ZnO bed) and still did not detect any arsine in the synthesis gas.

Following these tests, we removed the sorbent from the test bed and sent samples from the top, middle and bottom of the bed for chemical analysis (Figure 21). These analysis results suggested very small amounts of accumulation of arsenic, selenium and cadmium in the bed. We believe that it was not because the sorbent was not active in the removal of these contaminants but because there were only small amounts of these contaminants in the synthesis gas and the test duration was very short, resulting in very low accumulation of these contaminants in the bed.

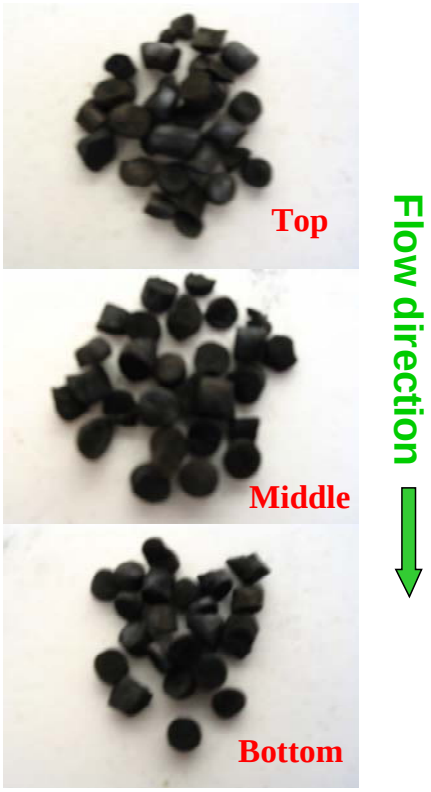

Figure 21. Sorbent samples removed from the different sections of the bed.

In January 2007, the PSDF attempted to continue with the gasification campaign. TDA personnel were available at the test site, unfortunately because of the gasifier problems the test was terminated.

3.2.4 PSDF Test Campaign #2

To support another test campaign TDA built two new sorbent reactors that were smaller in size (containing only 1/6th of the original sorbent volume). Small bed size was selected to ensure that we can observe the breakthrough and measure the breakthrough capacity of the sorbent. Figure 22 shows sketches of the reactor and the cross-section. We used a 1.5" Schedule 10 SS316 pipe (1.682" ID) with two welded end-caps for reactor construction. An internal

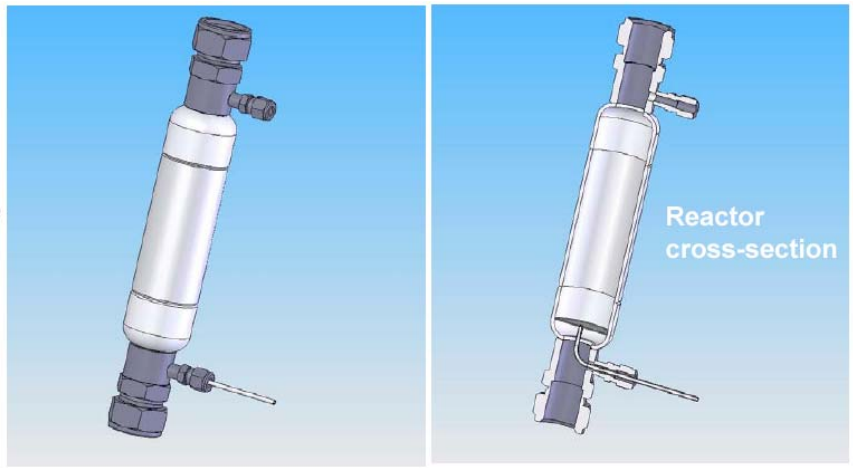

Figure 22. Sketches of the smaller reactors installed for PSDF Test Campaign #2.

steel frit was used to hold the sorbent particles in place. We used a smaller quantity of sorbent to observe trace metal breakthrough in relatively short duration to ensure the generation of useful data if the similar problems with feeding the low-grade lignite continues to plague the gasifier operation and causes pre-mature shutdowns.

In each bed, we loaded 126 g of sorbent in the form of 1/8" cylindrical pellets. Total calculated flow for the new beds is 31,189 SCF (bulk of this was flowed over the Bed A, 28,670 SCF). We measured the mercury concentration of the inlet gas using an Ohio Lumex Analyzer showing that the synthesis gas slipstream supplied to the test system contains about 2,900 ng/m^3 of Hg. Hg concentrations at the exit of the both beds were below the detection limit of the analyzer. As we did in our earlier test campaigns, we stored a large number of gas samples in Tedlar bags to analyze them using more sensitive Hg analyzers at our facilities. We also sent samples for analysis to an independent laboratory. For the analysis of other trace metals, we used chemical analysis, which will also be carried out by an independent laboratory.

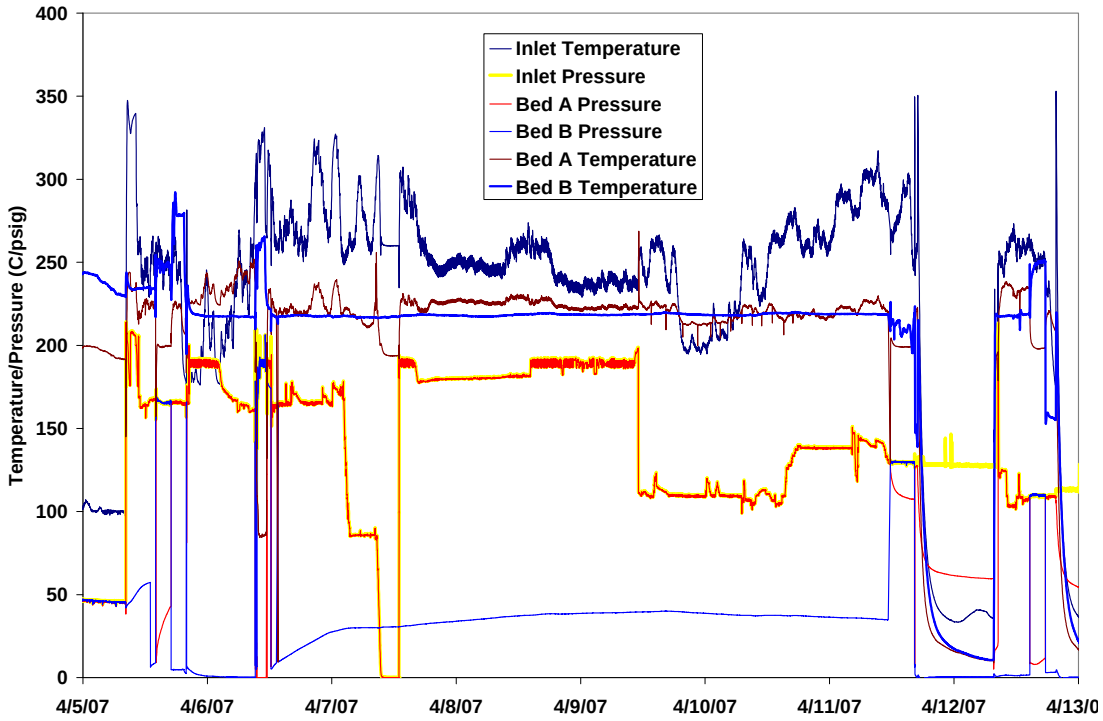

Figure 23. The test profile for the second test campaign at UNDEERC.

The second test campaign at the PSDF produced even less information than the first one. Because of the high sodium content of the lignite that was used for testing, the gasifier operation was highly unstable, and the TDA test skid received synthesis gas intermittently. We used primarily one of the sorbent beds during these tests to increase the overall amount of gas flow through the bed to ensure a high level of accumulation of trace metals. This would have provided us a better understanding about the ultimate capacity of the sorbent for these contaminants. Due to the high sodium levels in the synthesis gas, the mercury analyzers both malfunctioned (the sodium vapors covered the lamp and reduced the signal). For the measurement of capacity, we carried out post-reaction chemical analysis.

The chemical analysis results showed the highest loadings observed at the samples removed from the inlet section of the bed as 4.04 mg/kg, 58.2 mg/kg, 17.2 mg/kg and 13.1 mg/kg for mercury, arsenic, selenium and cadmium, respectively. Because of the relatively longer test duration, higher contaminant levels in the high sodium lignite and a smaller amount of sorbent used in the bed, we measured a higher capacity for the contaminants. However, as in the case of the first campaign, the measured capacity for these contaminants was only a small fraction of what we measured during the bench-scale tests at TDA because there was so little contaminant available for removal.

In summary, in the PSDF tests, the sorbent performance and the key aspects of our technology have been validated in two separate gasification campaigns. In these demonstrations, we showed the successful operation of the prototype test system at the conditions of interest, as well as the efficacy of sorbent in removing the trace metal contaminants. For instance, the sorbent reduced Hg concentration to less than 5 $\mu g/m^3$ for the entire duration of the tests, achieving over 99% Hg removal efficiency. Post reaction examination of the sorbent (via chemical analysis) also indicated the successful removal other trace metals (As and Se) from the synthesis gas (we did not observe any detectable Cd accumulation on the sorbent). Unfortunately, due to the relatively low concentration of the trace metals in the high sodium lignite feed (Falkirk lignite) and as a result of the intermittent operation of the PSDF gasifier (due to the difficulties in the handling of the low quality, high sodium lignite), only a small fraction of the installed sorbent capacity was utilized. We believe that although the feasibility and the technical viability of the concept were demonstrated, the data generated in these demonstrations may not reveal the full potential of the technology.

3.3 Demonstration Tests at UNDEERC

In an extension of the project, TDA carried out two more demonstration tests at UNDEERC's Gasification Facility using a slipstream of coal-derived synthesis gas provided from the Transport Reactor Demonstration Unit (TRDU) gasifier and a continuous fluidized-bed reactor (CFBR). The objective of the program was to extend our understanding and knowledge base on the novel trace metal removal sorbent, its integration capability on different gasifier types and its ability to handle trace contaminants from different types of coals. For these tests, two different types of coals were selected as the feedstock: Sufco (Utah) bituminous coal and Oak Hills (Texas) lignite. Previously, UNDEERC had been successful in feeding both of these coals into their gasifier and developed a good understanding and relevant data base on the synthesis gas composition generated by the gasification of these coals. Another objective was to gain information on the breakthrough capacity of the sorbent for mercury and other trace metals. In the earlier tests at the PSDF, due to premature shutdowns and limited on stream time we did not observe breakthrough of any of the target trace metal compounds from our sorbent bed. Hence it was our objective to identify the breakthrough capacity of the sorbent at least for mercury (due to the low sorbent capacity for Hg, we expected that the sorbent bed will be sized based on its mercury capacity).

Although our test skid was designed to American Society of Mechanical Engineers (ASME) pressure piping codes; because the electrical heaters or instrumentation were not rated to Division II Group B, the test skid was located outside the TRDU gasification tower area. TDA provided a stand-alone data acquisition system to measure operating parameters within the TDA test skid. All other data related to synthesis gas composition, temperature, pressure and contaminant concentration (Hg, Cl, S etc.) were monitored and logged by UNDEERC. In addition to the staffing required to operate the gasifier and auxiliaries (such as the desulfurization reactor), UNDEERC also provided a mercury analyzer and staffing necessary to conduct sampling for Hg. TDA provided two separate Hg analyzers to measure the Hg concentration within the system and to provide an independent comparison to that of the UNDEERC analysis. An on-line arsine analyzer was also in place to measure the efficacy of the sorbent in removing arsenic. We relied on post-test analysis of the sorbent samples for trace metal concentrations.

The first test campaign was conducted taking all of the gas flow from UNDEERC's CFBR while operating on a bituminous coal. A Utah bituminous coal from the Sufco mine was selected as the feedstock for this testing because of its favorable swelling characteristics. The second test campaign was conducted by taking a slipstream of the synthesis gas from the TRDU while operating on a Texas lignite from the Oak Hill mine near Henderson, Texas. This test was conducted as part of a different lignite gasification project that was also testing a sulfur removal sorbent, two water–gas-shift catalysts and a hydrogen separation membrane. TDA tests were piggy-backed on the testing being conducted for the UNDEERC client and neither TDA (nor the DOE project) paid for the operation of the TRDU gasifier. The UNDEERC report summarizing these tests is included in Appendix A.

3.3.1 CFBR Testing with Bituminous Coal

3.3.1.1 CFBR Preliminary Test Results

In these tests, UNDEERC also evaluated two other Hg sorbents, one commercial chlorinated activated carbon and an experimental metal-enhanced activated carbon. These two sorbents

were tested prior to our sorbent under identical conditions. The test duration for the commercial sorbents was set to 1 day, including the purging, heating, sorbent activation and temperature and pressure stabilization. The test duration for the TDA sorbent was set to 2 days with the anticipation that a higher capacity would be observed with the TDA sorbent. UNDEERC had extensive testing experience with various commercial and developmental sorbents through the activities funded by DOE and their commercial clients. Based on this prior experience, they were expecting Hg breakthrough from the bed to be observed within 24 hrs at the operating temperature (210°C), selected bed size and gas flow rate.

The results of the halogenated activated carbon and the metal impregnated carbon are shown in Figure 24. None of these sorbents were able to reduce the Hg concentration to low levels, while the metal enhanced activated carbon showed a relatively better performance. In these early tests, a steady baseline for Hg concentration was not achieved before the synthesis gas was diverted to the sorbent. The baseline measurement was 10 μg/Nm^3 at the beginning of the test. Some mercury removal was observed when the synthesis gas flow was directed to the carbon bed (Hg reduced to around 6 μg/Nm^3). The mercury levels then steadily rose to near 15 μg/Nm^3 before the packed bed was again bypassed. The second baseline indicated mercury levels from 15 to 25 μg/Nm^3.

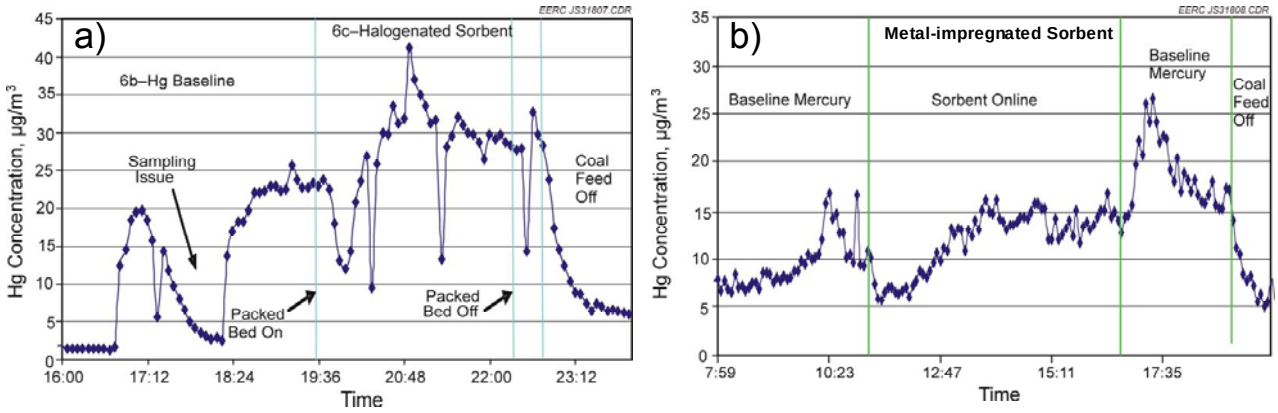

Figure 24. The Hg concentration at the exit of the carbon beds. T=210°C, P=100 psia, Hg Inlet = 10-25 μg/m^3 using coal-derived synthesis gas.

In the evaluation of TDA sorbent, the Hg concentration of the synthesis gas at the inlet of the sorbent bed was measured as 22 μg/m^3. Once a stable baseline measurement was established the synthesis gas was directed through the sorbent bed using a set of valves. The Hg concentration was much more stable because the unit was running for more than 2 days. Figure 25 shows the Hg removal concentration through the 6-hour test. The TDA sorbent reduced the Hg to less than 1 μg/m^3, achieving greater than 95% Hg removal efficiency. Unfortunately, the test was terminated pre-maturely before observing Hg breakthrough due to the problems at the coal feeder.

Although these tests showed that our sorbent can achieve a very high Hg removal efficiency and its superior performance against commercial and developmental sorbents (the other two carbon-based sorbents achieved only 25% Hg removal at best under the same conditions), due to the early shutdown, we could not assess the full Hg capacity of the sorbent. We measured 0.45 mg/kg (or 0.045% wt.) Hg capacity when the test was terminated. In a typical laboratory test at TDA, using simulated synthesis gas under representative conditions, we measure about

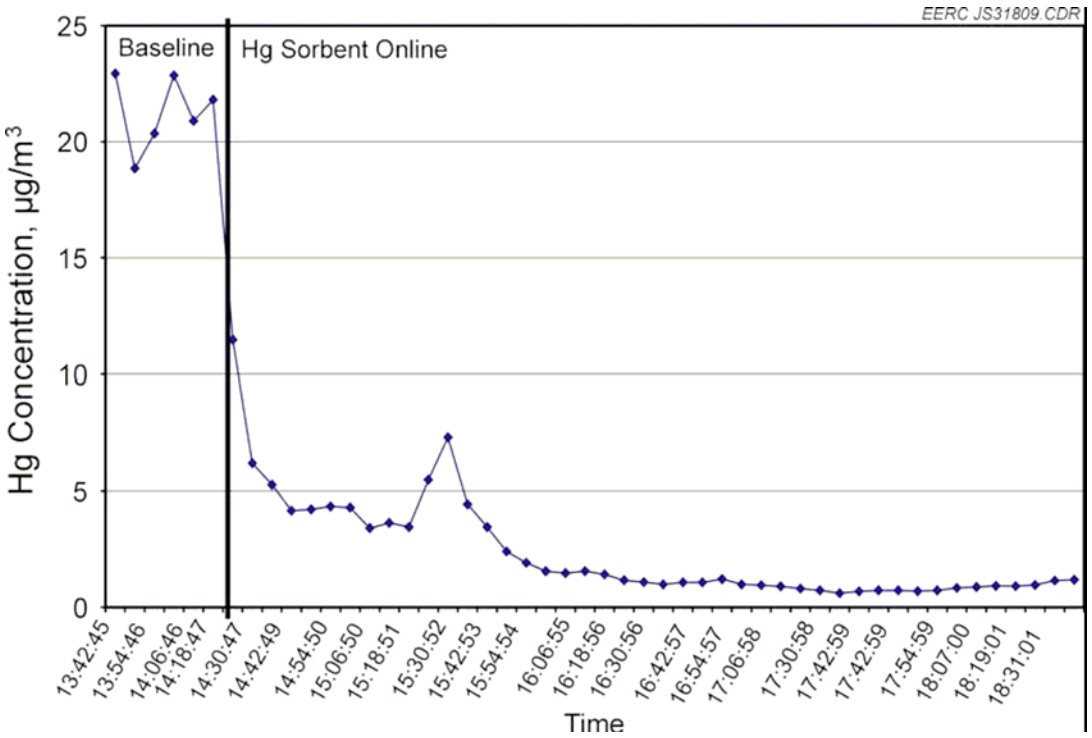

Figure 25. The Hg concentration at the exit of the TDA sorbent bed. T=210°C, P=100 psia, Hg Inlet = 22 µg/m^3 using coal-derived synthesis gas.

12 times increase in capacity. Considering that if the run was not terminated prematurely the sorbent would have achieved a much higher Hg capacity, we used the prior sorbent performance measured in the bench-scale tests at TDA as a basis to size the sorbent bed for the TRDU.

3.3.2 CFBR Tests on Bituminous Coal With The TDA Research Test Skid

Following the preliminary tests, we installed our test skid into the same location in the gas clean-up and processing train shown in **Error! Reference source not found.** where the fixed-bed evaluation was carried out. First, the operation of all system components (heaters, pressure control system etc.) had been evaluated at various operating conditions. In two test campaigns using different coals, the gasifier was operated both in an oxygen-fired and air-fired mode at different oxygen-coal–steam ratios. In each campaign TDA test skid treated at an average of 420 SCFH synthesis gas flow. In between the campaigns, the sorbent from the reactors was removed for evaluation. In the first test campaign, the CFBR was fed with the Sufco bituminous coal.

The goal of this test was to provide a low-sulfur synthesis gas feed to be tested using TDA's Hg, As, and Se removal test skid. As such, all tests were performed with the CFBR sending all of its synthesis gas to the sulfur reactor and HGFV before entering the fixed-bed TDA skid. The appropriate H_2S levels had to be achieved before feeding the synthesis gas to the TDA system. Tests were performed in air-blown mode with a separate recycled synthesis gas stream to provide the remaining gas needed to reach the desired test velocity, required to provide good flow to the TDA system and to maintain the bed velocity. The test plan was to operate the gasifier at a set test condition to provide a consistent synthesis gas composition to the test skid.

There were no specific test periods scheduled. However, data reduction and reporting is based on the time periods during which the TDA skid was online and the CFBR was operating at steady state and producing a synthesis gas with the required sulfur concentration.

The planned test duration was 5 days (starting May 24, 2008 and ending May 31, 2008), however due to two shutdowns resulting from problems with the coal feeder, the actual test time was much shorter (about 52 hrs). In this test campaign, we confirmed the operation of all system components and verified the effectiveness of all emergency procedures in the case of system malfunctions.

3.3.2.1 Coal Properties

The proximate–ultimate, x-ray fluorescence (XRF) ash, and heating value analyses for the Sufco coal are shown in Table 4. Table 5 contains the results of a trace metal analysis. The coal was sized to -10 mesh and premixed with either a combination of 5% wt. each of dolomite and kaolin or 5% wt. of only dolomite.

Table 4. Specifications of the Sufco bituminous coal used in the demonstration tests at UNDEERC.

Proximate Analysis, wt%	
Moisture	7.3
Volatile Matter	37.0
Fixed Carbon	48.3
Ash	7.4
Ultimate Analysis, wt%	
Hydrogen	5.53
Carbon	67.65
Nitrogen	1.4
Sulfur	0.34
Oxygen	17.68
Ash	7.4
XRF Ash Analysis, wt%	
SiO_2	44.3
Al_2O_3	10.8
Fe_2O_3	5.08
TiO_2	0.84
P_2O_5	0.24
CaO	12.2
MgO	1.85
Na_2O	4.23
K_2O	0.39
SO_3	20.0
Heating Value, Btu/lb	
Calc Calorific Value	11976

3.3.2.2 Operating Conditions

During testing, the quench pots and cyclone pot were emptied every hour and the filter vessel was back-pulsed and emptied periodically as the ΔP increased. Dräger tube measurements were taken every 1–2 hours at the gas chromatography (GC) and filter vessel to determine H_2S concentration. Sorbent was added to the sulfur reactor periodically to maintain solids inventory in the system. The finer particles had a tendency to escape the cyclone and end up in the filter vessel ash of the CFBR unit.

After approximately 15 hours of operation, the CFBR and sulfur reactor in conjunction, steady state and sufficient sulfur removal were achieved. At this time, flow to the TDA system was started. Steady state was maintained for 12 hours before cycling on the TDA skid deadheaded the system causing a major upset. After fixing the problem and again reaching steady state, the TDA system was brought back online for almost 2 hours before agglomeration in the gasifier caused another shutdown. The next steady-state period lasted about 12 hours and was only interrupted by a 30-minute period when the process control program of TDA system was updated. This test

Table 5. Contaminant concentration in Sufco bituminous coal.

	ppmv
Arsenic	0.35
Cadmium	0.03
Mercury	0.0381
Selenium	1.25

period again ended because of agglomeration issues in the CFBR. Following maintenance on the CFBR unit, steady state was achieved for over 24 hours, ending when the sulfur reactor auger failed. However, this period was broken up into three tests because of adjustments to the steam flow rate. Following repair of the auger, the unit was started up again, and the last test period lasted just under 4 hours.

As was stated earlier, the original plan was to use recycled synthesis gas along with supplemental nitrogen, but resulting from some problems with the recycle gas booster, recycle synthesis gas was off-line for a good portion of the run. In order to compensate for the lost gas velocity, nitrogen flow was increased, thus diluting the product gas; however, the net feed rate of the trace metals entering the TDA system with the coal remained approximately the same.

3.3.2.3 Results

The CFBR unit includes a data acquisition and control system that saves operating data every 30 seconds. These data include reactor temperatures; steam, air, oxygen and nitrogen flow rates; calculated fluidizing velocity; differential pressure across the bed; differential pressure across the filter vessel; and product gas composition. Table 6 shows the main steady-state operating conditions in the CFBR during each test period. The product gas composition was measured using a Yokogawa gas chromatograph, sampling and analyzing a point sample of gas every 10 minutes.

As was described earlier, the recycle synthesis gas was off-line for part of the test as indicated by the data presented in Table 6. In Table 6, Tests 2–5 show zero recycle gas flow and increased N_2 flow. Test 6 shows a very low recycle flow because the recycle booster pump was fixed toward the end of this test period and the recycle gas was back online. Table 6 shows an increased N_2 concentration during these tests because nitrogen flow was increased to maintain gas velocity in the CFBR unit.

Mercury concentration in the gas leaving the TDA unit was measured via a PSA Sir Galahad continuous emissions monitor (CEM). Table 8 shows the average mercury concentration and the baseline concentrations during each of the test periods. Mercury removal ranged from 80-90% and during the times when the TDA unit was on-line, Hg concentration was below 2 $\mu g/m^3$. Test 3 shows an Hg removal of 100%, but this is most likely inaccurate and is probably due to a problem with the CEM.

Table 7 shows the material balance data from the tests. Some discrepancies in the closure are because of accumulation or entrainment losses from the fluidized-bed reactor. No solids were added or removed from the bed itself during the testing. The low-carbon conversions achieved during this testing are primarily the result of low reactivity of the bituminous coal as compared to the more reactive low-rank coals typically tested, where 85% to 95% carbon conversion is more typical even when operating at the 1550°F maximum operating temperature. Higher-temperature operation, if it were possible in the CFBR, would result in better carbon conversion.

Table 6. Synthesis gas measurements and operating parameters during the first test campaign at UNDEERC.

Test No.	Avg. Bed Temp., °C	Steam Flow, g/hr	N_2 Flow, scfh	Recycle Syngas Flow, scfh	Oxygen Flow, scfh	Coal Feed, lb/hr	Superficial Gas Velocity, ft/s
1	794	923	137.5	250.0	32.0	1.99	0.905
2	803	951	193.2	185.6	28.9	2.06	0.895
3	792	1024	303.7	0.0	25.4	2.72	0.734
4	786	1017	318.1	0.0	25.4	2.50	0.849
5	793	1101	348.1	0.0	26.5	2.12	0.848
6	778	1702	317.3	77.1	28.4	1.80	0.920
7	772	740	108.3	266.1	31.1	2.75	0.856
8	776	936	107.9	263.9	31.1	2.75	0.855

Test No.	H_2, %	CH_4, %	CO %	CO_2, %	N_2, %	H_2S, ppm	HV, Btu/scf	N_2-Free HV, Btu/scf
1	6.29	1.40	3.38	6.10	77.16	22.3	45	199
2	4.91	0.56	0.06	2.32	92.22	15.5	22	281
3	7.08	0.75	0.38	2.67	87.49	41.0	32	254
4	6.52	0.64	0.02	2.53	88.68	24.7	28	245
5	5.13	0.52	0.00	2.45	90.53	14.9	22	232
6	5.12	0.54	0.04	3.30	89.85	41.0	22	219
7	5.95	1.46	1.57	7.26	74.51	112.5	39	154
8	9.81	2.06	5.38	6.82	72.31	14.3	70	253

Table 7. CFBR Operating Conditions.

Test No.	Coal Feed, lb/hr	Sulfur Sorbent, g/hr	Steam Flow, g/hr	Cyclone, g/hr	Cyclone LOI,[1] %	FV,[2] g/hr	FV LOI, %	Quench Pots, g/hr	Solid and Liquid Closure %	Solids CC, %
1	1.99	45	923	311	62.1	463	1.01	1024	101.3	71.6
2	2.06	47	951	474	70.8	411	1.01	775	90.6	52.9
3	2.72	62	1024	338	71.4	140	5.2	832	59.9	73.9
4	2.5	57	1017	507	62.3	140	5.2	889	73.6	63.1
5	2.12	48	1101	241	60.5	195	2.8	995	71.3	79.6
6	1.81	41	1702	273	60.5	262	2.8	1360	76.5	72.8
7	2.75	62	740	400	60.5	249	2.8	1203	96.7	74.1
8	2.75	62	936	499	78	450	18.6	1073	95.7	50.9

[1] Loss on ignition.

[2] Filter vessel.

Table 8. The average mercury concentration and the baseline concentrations during each of the test periods.

Test No.	Hg Baseline, µg/m^3	Hg Concentration, µg/m^3	% Hg Removal
1	7.10	0.67	90.56
2	7.21	1.08	85.02
3	9.55	0.00	100.00
4	8.47	1.24	85.36
5	8.47	1.36	83.94
6	8.47	1.34	84.18
7	8.47	1.63	80.76
8	NA	NA	NA

TDA supplied its own Hg analyzers to have an independent measurement of the Hg concentration as well as an on-line arsenic analyzer to continuously monitor the arsenic concentration at the inlet and exit of the sorbent bed. At the first day of the tests, the TDA analyzer measurements were in good agreement with UNDEERC's. TDA analyzer measured 11 mg/m^3 Hg concentration in the synthesis gas similar to that measured by the Sir Galahad. TDA sorbent removed more than 95% of the Hg from the synthesis gas.

At the end of the first day, when we attempted to switch the gas flow from one reactor to the other, our gas selection valve plugged and the whole flow was dead-ended (because all the synthesis gas output of the CFBR was diverted to the TDA test skid). This triggered an emergency gas vent upstream of our test skid, which caused the contents of the hot gas desulfurizarion system to be back-flushed into the hot gas filters. The problem was fixed promptly (a nitrogen back-pulse removed the sorbent from the filter elements and enabled flow), and the system was restarted. However, in the absence of desulfurization sorbent (since it is dislocated), a large amount of sulfur was introduced into our test skid, rendering the sorbent inactive. The large sulfur leakage also caused our Hg analyzer and arsenic analyzer to fail. In our skid we were using only small filter elements to remove any residual sulfur. These were overwhelmed with the large amounts of sulfur in the gas. Unfortunately, this incident occurred late at night and TDA personnel were not present at the test skid to isolate the test skid or the analyzers.

TDA's sorbent could remove mercury effectively provided that the sulfur concentration of the gas is 5 ppmv or less (the sorbent is designed to be located downstream of a bulk desulfurization sorbent). The gas analysis by UNDEERC suggests that the sulfur concentration of the synthesis gas exceeded 2,000 ppmv (the higher detection range of their analyzer).

The high levels of sulfur leakage also adversely affected the operation of our gas analysis system. It was our intent to carry out on-line Hg and arsenic measurements during these evaluations. TDA supplied a Genesys Labs Process Sentinel Hg analyzer equipped with a Cold Vapor Atomic Absorption Spectrometer with 0.1 µg/Nm^3 Hg detection capability to UNDEERC as a back-up Hg analyzer and a Honeywell Single Point Monitor for on-line arsenic measurements. Both analyzers failed due to the presence of high concentrations of sulfur in the synthesis gas (high sulfur levels were due to higher than expected sulfur leakage from the bulk

desulfurization bed). The sulfur eventually reached UNDEERC's mercury analyzer located at the end of the TDA test skid, and the Sir Galahad CEM also failed to produce consistent Hg measurements due to high sulfur concentrations.

Due to the lack of consistent on-line gas analysis, we relied on post-chemical analysis to observe the amount of contaminant accumulation over the sorbent. The elemental analysis results showed that the sulfur contaminated the entire sorbent bed in both reactors. As reported elsewhere, the TDA trace metal sorbent has an affinity for sulfur, forming a stable sulfide phase under the operating conditions of interest. Prior laboratory testing showed that our sorbent could achieve up to 20% sulfur loading on weight basis (lb of sulfur removed per lb of sorbent) comparable with that of the commercially available ZnO-based sorbents used in an expendable manner. When sulfur is present at low concentrations (5 ppmv or less) in the synthesis gas, the sorbent can provide sulfur polishing purifying the synthesis gas to levels acceptable for catalysts used for chemical synthesis processes (Fischer-Tropsch, methanol or water-gas-shift). At such low sulfur concentrations, the TDA sorbent can remove trace contaminants while removing sulfur. However, as the sulfur concentration goes beyond 5 ppmv, a separate sulfide phase forms which is inactive for the removal of trace metal species and renders the sorbent inactive.

Several samples were taken from the sorbent bed at different locations, and digested into an acid solution. The small amounts of the solution were then injected into an Inductively Coupled Atomic Absorption Spectrometer for Hg analysis. The Hg content of the sorbent at the inlet section of the bed exceeded 11 mg/kg, while the exit showed 6.8 mg/kg.

3.3.3 TRDU Slipstream Testing on Lignite With The TDA Research Test Skid

3.3.3.1 Equipment Description

The pilot-scale TRDU has an exit gas temperature of up to 980°C, a gas flow rate of 325 SCFM (0.153 m^3/s), and an operating pressure of 120 psig (9.3 bar). The TRDU system can be divided into three sections: the coal feed section, the TRDU, and the product recovery section. The TRDU proper, as shown in Figure 26, consists of a riser reactor with an expanded mixing zone at the bottom, a disengager, and a primary cyclone and standpipe. The standpipe is connected to the mixing section of the riser by an L-valve transfer line. All of the components in the system are refractory-lined and designed mechanically for 150 psig and an internal temperature of 1090°C. Detailed design criteria and a comparison to actual operating conditions on the design coal are given in Table 9.

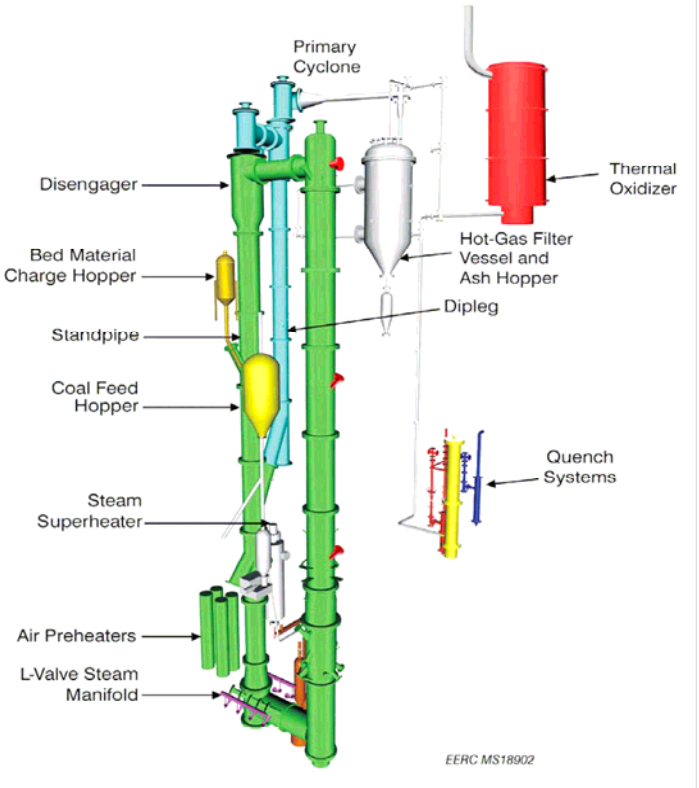

Figure 26. Schematic of the TRDU at UNDEERC.

Table 9. TRDU Operating Conditions.

Parameter	Design[1]	Actual
Coal	Illinois No. 6	Illinois No. 6
Moisture Content, %	5	8.5
Pressure, psig	120 (9.3 bar)	120 (9.3 bar)
Steam/Coal Ratio	0.34	0.34
Air/Coal Ratio	4	2.3
Ca/S Ratio, mole	1.5	2
Air Inlet Temperature, °C	427	380
Steam Preheat, °C	537	350
Coal Feed Rate, lb/hr	198 (89.9 kg/hr)	220 (99.9 kg/hr)
Gasifier Temperature, maximum °C	1010	950
ΔT, maximum °C	17	60 to 100
Carbon Conversion,[2] %	> 80	76.5
HHV[3] of Fuel Gas, Btu/scf (cor.[4])	100	110
Heat Loss as Coal Feed, %	19.5	13[5]
Riser Velocity, ft/s	31.3	25
Heat Loss, Btu/hr	252,000	450,000[5]
Standpipe Superficial Velocity, ft/s	0.1	0.38

[1] Kellogg, Brown, and Root (KBR) design specifications.
[2] Carbon conversion = (wt carbon feed − wt carbon removed)/wt carbon feed × 100.
[3] Higher heating value.
[4] Corrected.
[5] Higher coal feed rate and lower air and steam preheat resulted in lower percent heat loss but higher net heat loss.

The solid feedstock to the transport reactor can be admitted through three nozzles, which are located at varying elevations. Two of these nozzles are located near the top of the mixing zone (gasification mode), and the remaining one is near the bottom of the mixing zone (combustion mode). During operation of the TRDU, feed is admitted through only one nozzle at a time. The feed rate is controlled by a revolutions-per-minute (rpm) metering auger and monitored by the coal addition rates to the pressurized feed hoppers. Oxidant is fed to the reactor through two pairs of nozzles at varying elevations within the mixing zone.

For the combustion mode of operation, additional nozzles are provided in the riser for feeding secondary air. Hot solids from the standpipe are circulated into the mixing zone, where they come into contact with the air/nitrogen and the steam being injected into the L-valve loop seal. This feature enables spent char to contact steam and oxygen prior to the fresh coal feed. This staged gasification process enhances process efficiency. Gasification or combustion and desulfurization reactions are carried out in the riser as coal/biomass, sorbent, and oxidant (with steam for gasification) flow up the reactor. The solids circulation into the mixing zone is controlled by fluffing gas in the standpipe, L-valve aeration flows, and the solids level in the standpipe.

The riser, disengager, standpipe, and cyclones are equipped with several internal and skin thermocouples. Nitrogen-purged pressure taps are also provided to record differential pressure across the riser, disengager, and cyclones. The data acquisition and control system scans the data points every 0.5 s and saves the process data every 30 s. The bulk of entrained solids leaving the riser is separated from the gas stream in the disengager and circulated back to the riser via the standpipe. A solids stream is withdrawn from the standpipe via an auger to maintain the system's solids inventory. Gas exiting the disengager enters a primary cyclone. Gas exiting this cyclone enters a series of jacketed-pipe heat exchangers before entering the HGFV. The cleaned synthesis gas leaving the HGFV is depressurized and combusted in a thermal oxidizer. Heat and material balance data from around the thermal oxidizer provide an additional measure

of carbon conversion and sulfur removal. Even with the large amount of nitrogen purges and relatively high heat losses, the fuel gas from the TRDU is of generally sufficient quality to sustain combustion in the thermal oxidizer without the requirement of supplemental fuel.

3.3.3.2 Test Plan

The goal of this test was to provide a synthesis gas slipstream from the TRDU to the gas clean-up and processing train where several warm-gas cleanup technologies were tested, including the transport reactor for sulfur removal and TDA's skid for mercury and trace element control. The process schematic is shown in Figure 27. All warm-gas cleanup procedures were performed at temperatures over 205°C. Flow was opened to the warm-gas cleanup units once a baseline steady state on the TRDU was achieved. Each unit in Figure 27 was brought online individually to determine a new baseline for each step in the process train. As was done during the CFBR synthesis gas test, gas was not allowed to flow through the TDA system until sulfur removal in the transport reactor desulfurizer was sufficient.

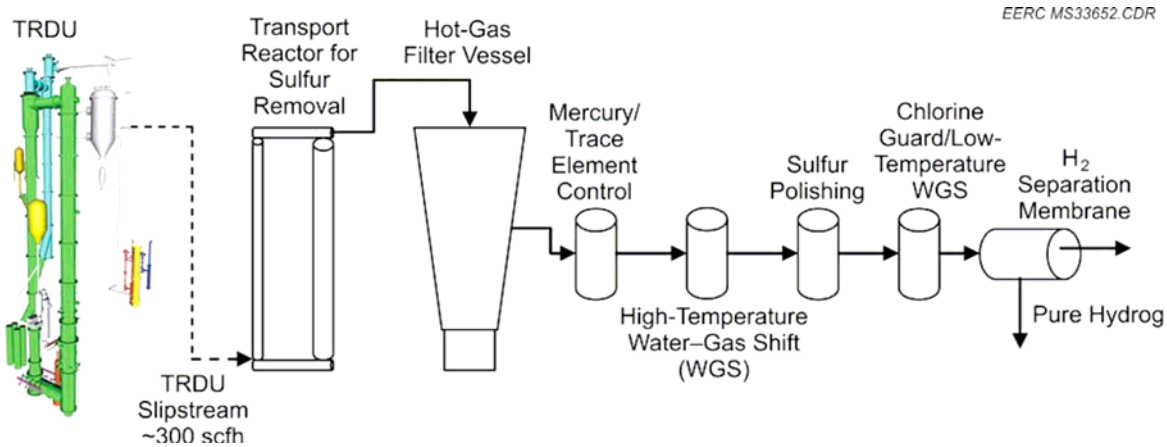

Figure 27. The schematic of the gas processing and clean-up train in the second test campaign at UNDEERC.

3.3.3.3 Coal Analysis

Proximate–ultimate, XRF analysis (XRFA), and heating value analyses for the Oak Hill lignite used during this test are located in Table 10. Table 11 contains the trace metal concentrations of interest.

3.3.3.4 Results

While the TRDU had 16 scheduled test periods, there were only 10 test periods identified on the warm-gas cleanup end of the process, which were divided by changes in the process train flow. Table 12 and Table 13 shows the TRDU slipstream composition at the inlets of the sulfur reactor and TDA skid during each of the 10 test periods. During the start-up and stabilization and shutdown of the gasifier, TDA test skid (and the whole gas clean-up and processing train) did not receive any synthesis gas.

Table 10. Specifications of the Oak Hills lignite used in the demonstration tests at UNDEERC.

	As Received	Air Dried
Proximate Analysis, wt%		
Moisture	32.4	28.6
Volatile Matter	26.2	31.38
Fixed Carbon	31.45	30.96
Ash	9.95	9.07
Ultimate Analysis, wt%		
Hydrogen	6.65	6.44
Carbon	44.07	45.78
Nitrogen	0.95	1.07
Sulfur	0.69	0.72
Oxygen	37.69	36.92
Ash	9.95	9.07
XRF Ash Analysis, wt%		
SiO_2	48.0	48.0
Al_2O_3	23.8	23.8
Fe_2O_3	8.78	8.78
TiO_2	1.12	1.12
P_2O_5	0.16	0.16
CaO	12.8	12.8
MgO	3.77	3.77
Na_2O	0.44	0.44
K_2O	1.12	1.12
SO_3	–	–
Heating Value, Btu/lb	6205	7743

Table 11. Specifications of the Oak Hills lignite used in the demonstration tests at UNDEERC.

Arsenic	1.27 µg/g
Cadmium	0.20 µg/g
Mercury	0.186 µg/g
Selenium	7.71 µg/g

Mercury concentration was analyzed at the outlet of the TDA system via a CEM. Figure 28 depicts a typical mercury concentration versus time data curve taken during Test 6 (longest duration) of the warm-gas cleanup process. This figure shows that while the TDA system was online, Hg concentration was less than 10 µg/m^3. The figure also shows that when the system was taken off-line, Hg concentration increased dramatically to a baseline of roughly 40–50 µg/m^3. Table 14 shows the average mercury baseline and concentration during each of the 10 test periods. This data is representative of the time during each test period when the TDA skid was online. The TDA skid was closed to flow during Tests 1, 2, and 7, but during the other test periods, mercury removal ranged from 97.3%–99.9%. Test 9 was lower than this range because the TDA skid was only online for a short time during this period and did not reach steady state before being taken off-line.

Table 12. TRDU slipstream composition at the inlet of the sulfur reactor during each of the 10 test periods.

Test No.	H_2, %	CO, %	CO_2, %	N_2, %	CH_4, %	H_2S, ppm
1	7.06	5.10	15.83	68.28	3.73	3570
2	9.40	5.66	13.66	67.15	1.79	1312
3	8.51	4.86	15.34	69.50	1.74	2947
4	8.87	4.97	15.50	68.25	1.83	1938
5	9.45	5.77	15.37	66.71	1.97	1996
6	9.46	6.61	14.81	66.87	1.75	1906
7	15.38	7.22	21.54	53.37	2.57	2988
8	18.63	7.67	24.71	45.81	3.17	3622
9	17.65	7.57	25.27	46.72	3.00	3330
10	18.88	8.83	25.59	44.70	3.10	3304

Table 13. TRDU slipstream composition at the inlet of the TDA skid during each of the 10 test periods.

Test No.	H_2, %	CO, %	CO_2, %	N_2, %	CH_4, %	H_2S, ppm
1	8.29	4.77	15.03	69.08	1.66	3455.47
2	7.68	4.38	13.83	72.34	1.53	0.59
3	10.89	0.99	16.66	68.58	1.49	0.67
4	11.45	1.00	17.03	67.63	1.61	0.00
5	13.34	0.14	18.41	65.49	1.61	0.00
6	13.69	0.49	19.92	67.23	1.63	0.04
7	17.51	7.95	24.53	55.87	3.09	24.19
8	21.83	1.42	27.91	47.06	2.93	83.89
9	19.72	0.63	27.18	48.95	2.51	0.00
10	20.61	1.41	28.36	47.22	2.68	0.00

Table 14. The average mercury baseline and concentration during each of the 10 test periods.

Test No.	Hg Baseline, $\mu g/m^3$	Hg Concentration, $\mu g/m^3$	% Removal
1	NA	NA	TDA off-line
2	NA	NA	TDA off-line
3	21.5	0.31	98.56
4	21.5	0.075	99.65
5	21.5	0.018	99.92
6	41.8	1.13	97.30
7	54.7	54.7	TDA off-line
8	56.6	0.108	99.81
9	45.1	6.78	84.97
10	55.8	0.436	99.22

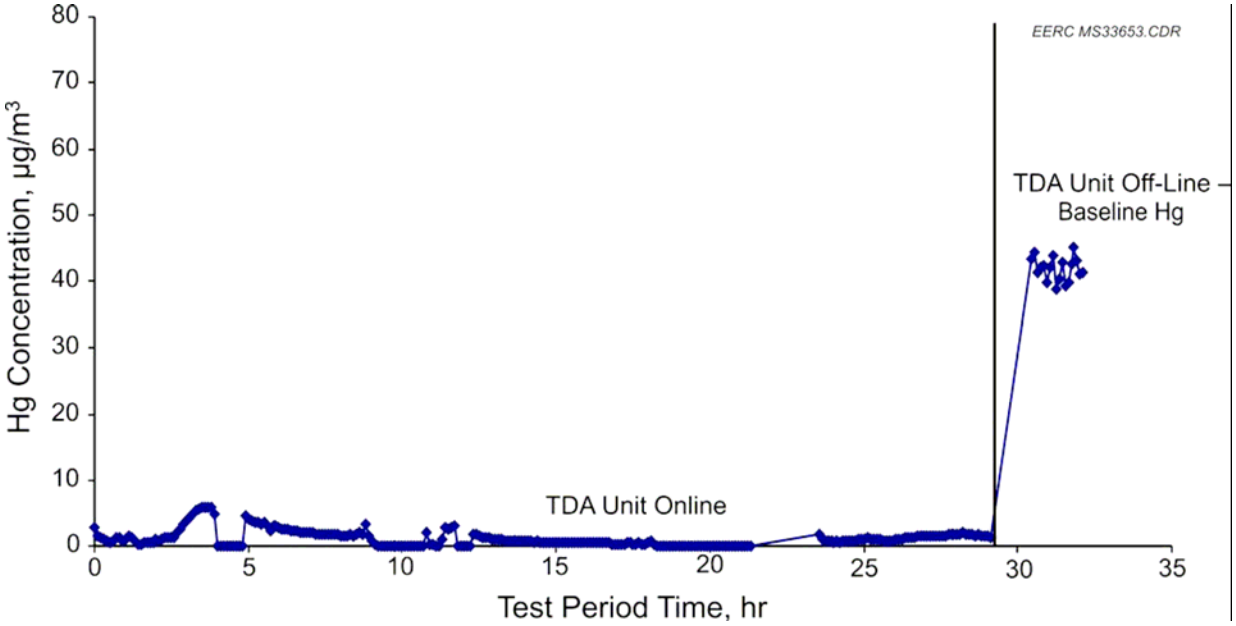

Figure 28. The Hg concentration at the exit of the TDA sorbent bed. T=410°F, P=100 psia, Hg Inlet = 40-50 µg/m^3 using coal-derived synthesis gas (UNDEERC data).

In this second test campaign (June 9 through June 14, 2008), TDA test skid treated slightly less than 40,000 CF of coal-derived synthesis gas. In our test skid, we used two sorbent beds that were exposed to the synthesis gas for pre-determined durations. We operated one of the sorbent beds (referred to as Bed A) at 260°C and the other bed (Bed B) at 210°C. We operated the two sorbent beds at two different temperatures to identify the impact of temperature on performance. It is well known that Hg affinity to any solid surface is greatly reduced as temperature increases. Like other sorbents, we realize that our sorbent's ability to remove Hg (i.e., Hg capacity) will decrease by increasing temperature. In order for the gas clean-up process to be cost-effective, we believe this bed must be operated in a regenerable manner to increase sorbent utilization and to reduce the sorbent replacement cost. TDA developed a proprietary gas clean-up process that allows the removal of mercury in a regenerable manner while irreversibly removing all other trace metal contaminants. Hence, to increase the utilization of the sorbent, we investigated the potential of regenerating and reusing the sorbent. For sorbent regeneration, a mild temperature swing was applied, heating the reactor to ~285°C. During regeneration, the operating pressure of the bed was also reduced to ambient pressure to be able to facilitate the desorption of mercury. The second bed was maintained at 210°C throughout the test duration. Because the temperature for Bed B was favorable for the sorbent to achieve a high Hg capacity no regenerations were attempted. We believe that both of these operating temperatures are feasible for different types of gasifiers, ensuring operation above the dew point of the synthesis gas. For GE gasifiers with water quench operating temperature of 260°C is feasible, while for the transport gasifier which produces a low moisture content synthesis gas operating the bed at 210°C eliminates any water condensation.

Figure 29 shows the operation sequence for Bed A and Bed B throughout the test. While Bed A was under regeneration, the Bed B was online and removing contaminants from synthesis gas. The overall synthesis gas flow rate into the test skid was 500 SCFH throughout the test. Bed A was online for 45.5 hrs while Bed B was online 34.3 hrs treating 22,750 CF and 17,150 CF synthesis gas, respectively (each bed contained 200 mL of sorbent).

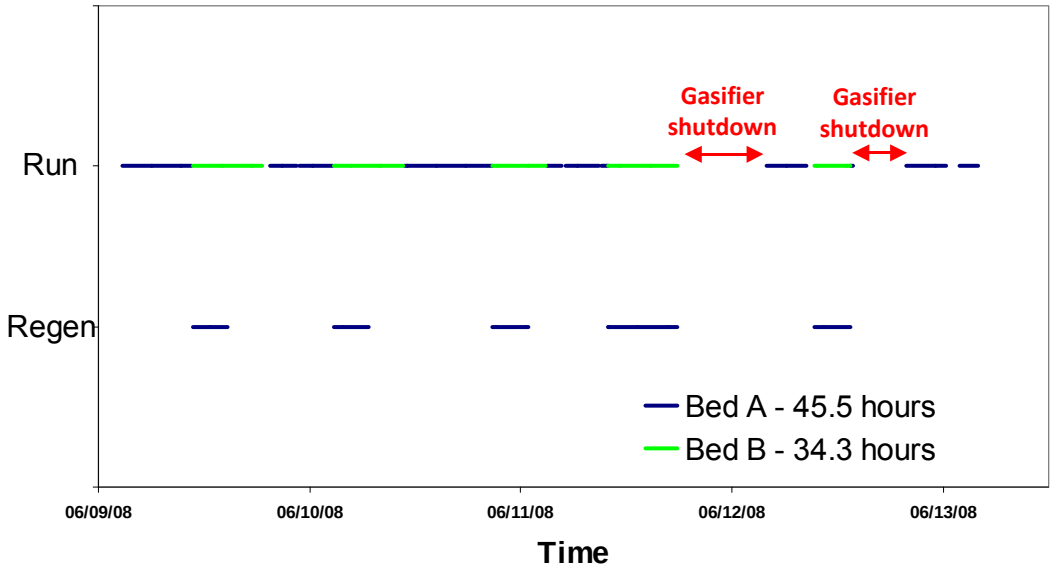

Figure 29. The test sequence for the beds during the second test campaign at UNDEERC.

Figure 30 shows a typical temperature and pressure profiles for the low temperature bed (Bed B). When it was not under operation, we maintained the Bed B at the temperature of operation (210°C) using external heaters, so when the gas was directed to the bed it remained at the desired temperature. When Bed A (the high temperature bed) was not in operation, we were carrying out regeneration. Throughout the test duration, we had either Bed A or Bed B on-line, removing contaminants from synthesis gas.

UNDEERC has measured the Hg concentration of the synthesis gas at the inlet and at the exit of our system. Because a bed was on-line all the time and both beds worked successfully, they reported a high Hg removal efficiency by our test skid at all times during testing (Figure 28).

Figure 31 shows the temperature profiles for Bed A during the regeneration process. We selected different regeneration temperatures. Because the bed was undergoing a temperature cycle, and the gas flow rates during absorption and regeneration were different, the temperature control in the bed was more challenging and the temperature profiles were not as smooth as in the case of Bed B. Obviously, it is desirable to maintain a small temperature differential between the absorbing and regenerating beds to minimize the heat input to the system. We carried out limited tests to determine the impact of regeneration temperature and duration on sorbent performance.

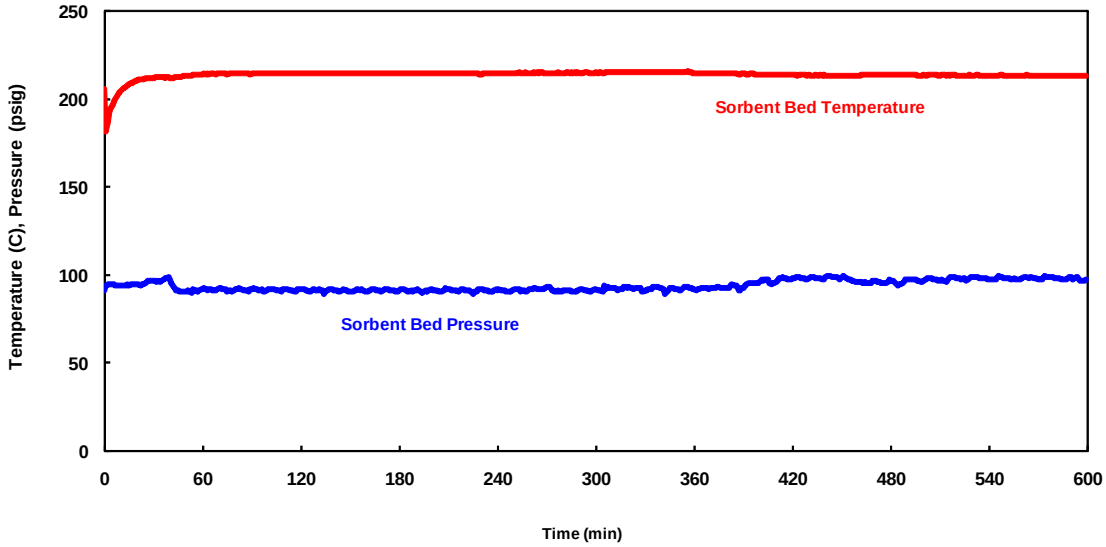

Figure 30. The temperature and pressure profiles of Bed B through a 10 hr test period during the second test campaign at UNDEERC.

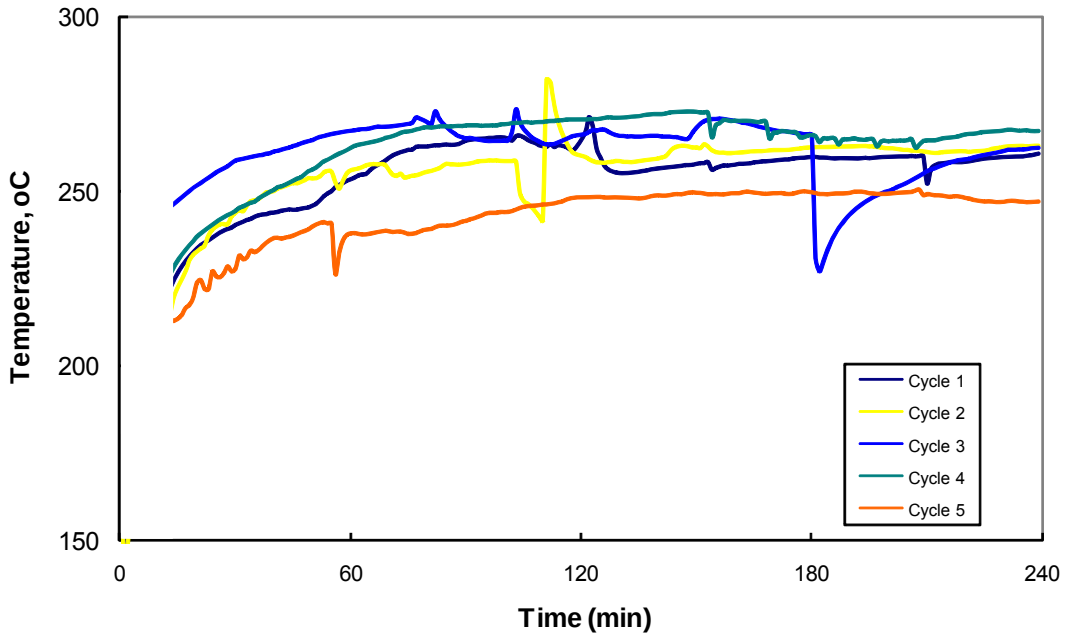

Figure 31. The temperature profiles during the regeneration of Bed A throughout 5 cycles in the second tests campaign at UNDEERC.

Figure 32 shows the Hg regeneration profile as a function of time for Cycle #1 and Cycle #3. The Hg capacity of the sorbent in the first cycle was far greater than the regenerated sorbent in agreement with our bench-scale experiments at TDA's facilities. We believe that using a mild temperature swing does not drive all the Hg off the sorbent but it still allows the sorbent to maintain a reasonable working capacity. These results show the feasibility of the concept demonstrating that the Hg can be removed from the sorbent under mild conditions. As indicated by the data analysis performed by UNDEERC, the Hg leakage from both sorbent beds was greater than 90% throughout the test. This indicates that the TDA sorbent can operate in a regenerable manner, a particular advantage to ensure cost effective operation at 500°F.

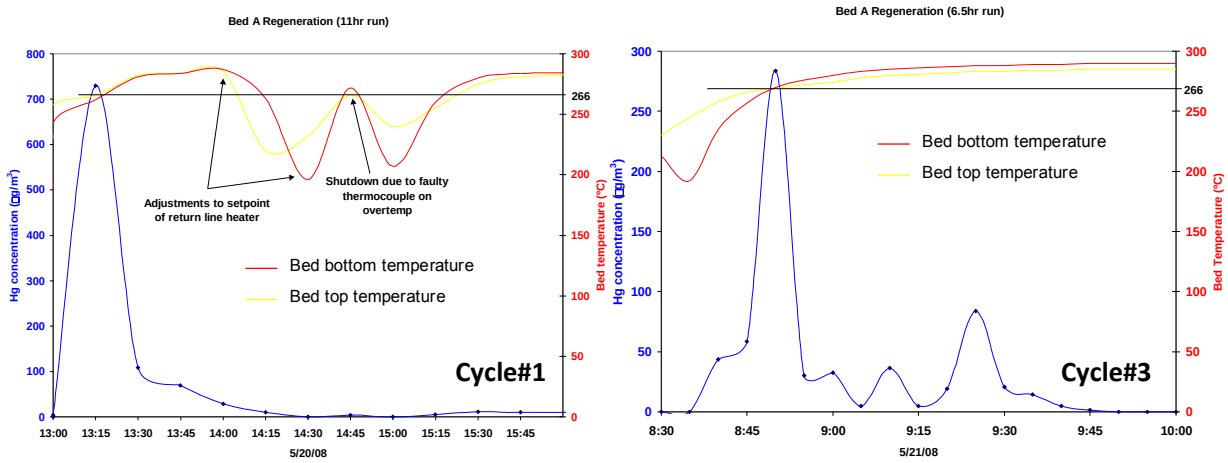

Figure 32. Hg concentration profiles during the regeneration of Bed A for Cycle#1 and Cycle #3.

3.3.3.5 Chemical Analysis Results

After the high temperature mercury removal testing was completed the mercury sorbent was removed from the beds. Three samples were taken from both Bed A and Bed B, one from the top of the bed, one from the middle of the bed and one from the bottom of the bed. These samples were sent out for chemical analysis. The results are shown in Figure 33. The mercury levels were considerably higher in Bed B. This result is expected because Bed A was regenerated throughout the testing, removing the mercury periodically from the sorbent bed. Bed B was not regenerated so all of the mercury adsorbed throughout

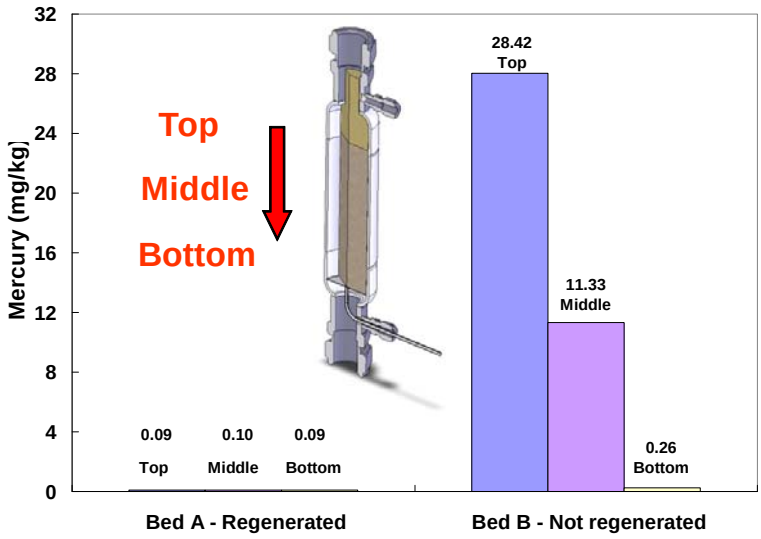

Figure 33. Chemical analysis results showing mercury accumulation at the inlet, middle and bottom section of the bed observed during the second gasification campaign at UNDEERC.

the five days of testing was present on the sorbent. However, the levels of mercury detected by the chemical analysis were lower than expected. Based on the amount of gas treated (12,723 SCF) and assuming an average Hg inlet concentration of 22 μg/m^3 throughout the test and 95% Hg removal efficiency, we expected that the Hg concentration of the spent sorbent removed from the bed should be about 44.01 mg/kg. For the sample recovered from the inlet section of the bed, we measured 28.42 mg/kg (for the entire bed a much lower average Hg loading of 13.34 mg/kg was calculated). Considering the Hg loading only on the inlet section of the bed (since the low numbers at the bed bottom were skewing the average), about 35% of the Hg fed into the bed was not accounted for. We attribute the lack of Hg mass closure to the errors that may incur during the chemical analysis, the possible variation in the Hg concentration of the synthesis gas at the bed inlet, and the moisture and oxygen adsorption on the spent sorbent samples after they are removed from the bed to sent for chemical analysis (adsorption of moisture and oxygen could dilute the Hg and other contaminant concentrations).

Figure 34 shows the arsenic and selenium concentrations measured in the sorbents. Bed A and Bed B show comparable amounts for both contaminants indicating that they were not removed during the regeneration process.

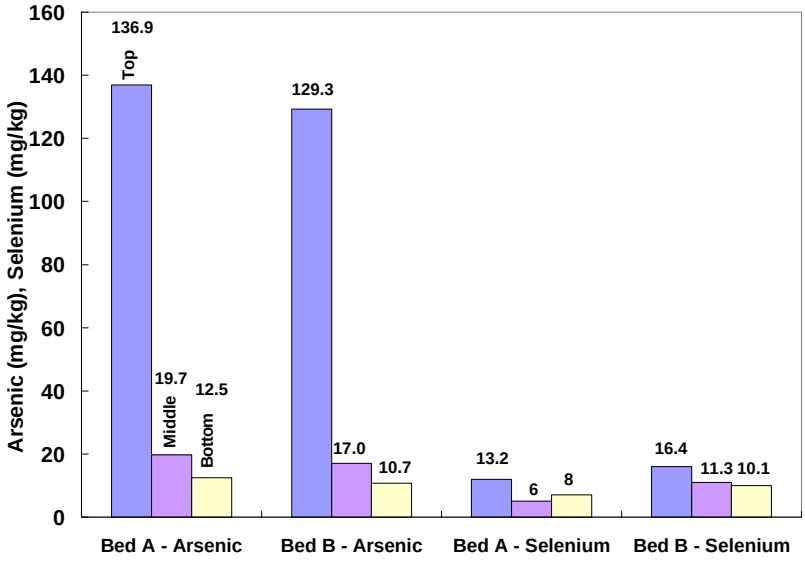

Figure 34. Chemical analysis results showing arsenic and selenium accumulation at the inlet, middle and bottom section of the bed during UNDEERC Test Campaign #2.

In our bench-scale experiments, we measured much higher capacity for our sorbent in arsenic and selenium removal. In the lab, in the absence of sulfur, we measured up to 10% wt. (lb of arsenic per lb of sorbent) capacity for arsenic and selenium, while in these tests, we measured at most 0.014% wt. arsenic capacity (the sample taken from the inlet section of the bed). These results were somewhat expected. For these experiments, we designed the beds for Hg removal, which is the most difficult trace metal contaminant to remove from the synthesis gas at high temperatures. And since there was excess sorbent capacity for As and Se, we were not expecting the breakthrough of these contaminants from our sorbent beds. To measure the arsenic capacity of the sorbent, TDA is in the process of carrying out a demonstration test with Eastman Chemicals at their coal-to-chemicals plant at Kingsport, TN under a separate SBIR project ("Control of Catalyst Poisons from Coal Gasifiers" Grant No. DE-FG03-01ER83308). We use 500 cc sorbent bed to treat a 5 times greater synthesis gas flow for over 70 days with synthesis gas containing two orders of magnitude higher arsenic concentration to be able to observe the breakthrough.

Overall, these results indicate that it is feasible to develop a multi-contaminant sorbent that is effective at high temperatures. This sorbent can be operated in a regenerable manner to

remove Hg from the bed, while irreversibly removing arsenic and selenium with high capacity (we have no conclusive results for cadmium).

3.3.3.6 Leaching Tests – Synthetic Groundwater Leaching Procedure (SGLP)

We performed measurements to evaluate the stability of Hg over the sorbent evaluated at the second campaign at UNDEERC. It is likely that the spent sorbent used in the synthesis gas clean-up will be disposed as a hazardous waste at the end of its life. We believe it will be classified hazardous not because the ingredients in the sorbent are hazardous but because of the absorbed contaminants. Once the sorbent is landfilled, it is important that the absorbed species to remain on the sorbent and not to leach into the ground water or into the habitat. Mercury fate over absorbents was the subject of previous studies and an ASTM method has been established (all the literature was based on evaluation of the fate of mercury from sorbents used to control mercury emissions from the flue gases of the pulverized coal combustion plants). The stability of the absorbed mercury on the sorbent is a factor to be considered in the sorbent selection for mercury abatement. There are a large number of leaching methods available that have been developed and tested during the past 40 years. Hassett (1987) provided a leaching method (Synthetic Groundwater Leaching Procedure – SGLP) and compared its use with results from the EPA-EP, the TCLP, and an ASTM procedure, concluding that leaching tests should be matched to field conditions. A later report by Hassett (1998) included a discussion in greater depth of the importance of matching a procedure's leaching solution to the intended future environment of a material.

We carried out similar tests to evaluate the stability of mercury over the spent sorbent tested at UNDEERC. Because no literature existed for other species, we only investigated the stability of mercury (we also have evidence to believe that among other contaminants, mercury is more prone to leaching if the sorbent is landfilled).

We sent mercury-laden samples to an independent lab to determine the permanence of the mercury on the sorbent using the SGLP (Hassett 1998). This procedure exposes the fly ash containing the mercury-laden sorbent to a synthetic groundwater. Three different lengths of tests may be performed. The groundwater generally contains Na, SO_4, and HCO_3, as well as other minerals that may be present in the groundwater of the location of interest where the fly ash is to be stored, disposed of, or used. The pH is adjusted to mimic the groundwater where the fly ash is to be stored, disposed or used. Three different lengths of tests may be performed. The shortest test is 18 hours, during which the fly ash is exposed to the synthetic groundwater in a 20:1 liquid: solids ratio, with end-over-end agitation. At the end of 18 hours, the mixture is filtered, and the liquid analyzed for the presence of mercury, or other metal species of concern. The longer tests are conducted for 30 or 60 days, with the same procedure.

Table 15. SGLP Test Conditions.

SGLP Test Conditions			
Sorbent amount used		0.6	g
DI water used for		12	mL
for leaching			
Amount present in the sorbent			
Hg Present	0.6	mg	0.1%

Our Hg sorbent taken after the adsorption test containing 0.1% adsorbed Hg was mixed with deionized (DI) water in the ratio of L/S = 20. The sorbent water mixture was agitated for 18 hr and filtered using a Millipore Type AW prefilter, AW0304700. The leachate (filtrate – DI water) was then sent to Huffman Laboratories in Golden, CO for analysis of Hg and the active materials present in the sorbent. A control sample of the DI water used was also sent to the

laboratory for getting a baseline. The SGLP test conditions are summarized in Table 15. The test results from Huffman Laboratories are provided in Table 16. The absorbed Hg is held strongly on TDA's sorbent and only leached a very small amount, while the active materials did not leach from the sorbent surface. These results prove that TDA's Hg sorbent is stable after Hg absorption and does not leach into the ground water.

Table 16. SGLP Test Results.

Element	Present in leachate (ppm)	Max. Possible (ppm)	% leached
Hg	0.52	50	1.04%

3.4 Engineering and Cost Analysis

Finally, we included a preliminary economic analysis for our sorbent-based trace metal removal technology. As part of the DOE Phase II SBIR project ("Sorbents for Mercury Removal from Coal Gasifier Effluents" Grant No. DE-FG03-02ER83551), TDA carried out a cost analysis for its trace metal removal system from coal-derived synthesis gas. The results of this analysis are provided in Appendix B. As part of this project, we were planning to update this analysis using the sorbent capacity measured for the trace metal contaminants during the demonstration tests. However, because these field tests did not reveal any addition information on sorbent capacity (rather showed the technical feasibility of the concept and shed light to the fact that a very high Hg removal efficiency can be achieved at high temperatures for a number of synthesis gas streams generated by the gasification of different types of coal), we relied on the capacity data measured in our bench-scale experiments and retained the cost analysis results reported under the SBIR project. Based on major cost items, such as annualized capital cost, operating and maintenance expenses and sorbent replacement costs, we estimated the cost of mercury removal as $2,995/lb. This analysis assumes that the cost of removal of all other trace metal contaminants is included in this cost. At this cost, the incremental cost increase due to mercury control in an advanced gasification combined cycle power generation system is estimated as 0.23 mills/kWh, an increase of less than 1% over the cost of energy (which is assumed to be 35 mills/kWh). Thus, effect of mercury removal to the cost of electricity using our high temperature cleaning process will be fairly small. We believe that the cost of the trace metal removal system will be dominated by the cost of removal of mercury due to the low capacity of the sorbents for mercury. Thus, the proposed costs will also cover the cost of removal of all other trace metal contaminants.

3.5 Conclusions

As part of the test program, we carried out four demonstrations at two different sites using the synthesis gas generated by the gasification of various lignites and a bituminous coal. Two of these tests were conducted at the Power Systems Demonstration Facility (PSDF) in Wilsonville, Alabama; a Falkirk (North Dakota) lignite and a high sodium lignite (the PSDF operator Southern Company did not disclose the source of this lignite) were used as the feedstock. In collaboration with the University of North Dakota Energy Environmental Research Center (UNDEERC), we also carried out two more demonstrations using synthesis gas slipstreams generated by the gasification of Sufco (Utah) bituminous coal and a Oak Hills (Texas) lignite.

Overall, the test results indicate that TDA sorbent is capable of removing multi-contaminants in the coal-derived synthesis gas at high temperature. TDA sorbent successfully removes Hg from the synthesis gas streams generated by different gasifiers using different coals at different sites and achieve greater than 95% Hg removal efficiency at 260^{o}C. This sorbent can be operated in a regenerable manner to remove Hg from the bed, while irreversibly removing all other trace metals with high capacity. The fate of mercury has been evaluated in a Synthetic Ground Water Leaching Procedure Test, and has been shown that it will remain on the sorbent once the sorbent is disposed.

Based on a preliminary engineering and cost analysis TDA estimated that the cost of mercury removal from coal-derived synthesis gas as $2,995/lb (2002 dollars). This analysis assumes that the cost of removal of all other trace metal contaminants is included in this cost. The projected cost will result in an increase of less than 1% over the cost of energy.

3.6 Recommendations

The DOE project provided enormous insight in developing an understanding and knowledge base on our novel trace metal removal sorbent and gas clean-up process and confirm its performance capabilities while treating actual coal-derived synthesis gas. The synthesis gas generated at the test sites were highly representative of commercial gasification technologies that enabled evaluation of the sorbent under highly relevant conditions.

A major problem observed during the demonstration tests was related to the limited duration and intermittent operation of the pilot-scale gasifiers (because it is expensive to operate them for long durations). It is recommended that the performance of the sorbent be evaluated for longer durations to gather more information on the breakthrough of metal contaminants in addition to mercury. Longer test durations will also allow us to demonstrate the regeneration capability of the sorbent for more cycles (in current tests, we demonstrated 5 cycles).

The TDA design involves the use of semi moving-bed reactors to house the sorbent. By always providing a fresh batch of sorbent at the reactor exit, the moving-bed reactors ensure high removal efficiency of the contaminants. The spent sorbent removed from the reactor has the longest exposure to the contaminants at high concentration, which increases its utilization. Thus, it is recommended to demonstrate the sorbent performance in a semi moving-bed reactor.

Finally, a detailed cost analysis must be carried out to fully assess the benefits of the new technology. The preliminary cost analysis carried out in this and earlier projects was highly limited in scope. A detailed and preferably an independent cost analysis must be carried out to evaluate the economic impact of the new technology.

4. Appendix A: UNDEERC Report

TESTING OF TDA RESEARCH SYNGAS CLEANUP SORBENTS

Final Report

(for the period May 1 through October 31, 2008)

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TESTING OF TDA RESEARCH SYNGAS CLEANUP SORBENTS

OBJECTIVES AND GOALS

The Energy & Environmental Research Center (EERC), under a subcontract to TDA Research, Inc., tied in a test skid to test various TDA Research sorbents for their ability to remove the trace metal contaminants such as mercury, arsenic, selenium, and cadmium. The objectives of the project were to conduct two different test campaigns that would generate and supply actual coal-derived syngas to the test stand built, supplied, and staffed by TDA personnel. TDA's test skid was originally designed to handle no more than 100 scfm of fuel gas at 120 psig and at temperatures in the range of 500° to 700°F; however, this system was since modified to accept much smaller flow rates. This skid was designed to American Society of Mechanical Engineers (ASME) pressure piping codes; however, electrical heaters or instrumentation were not rated to Division II Group B, thus requiring that the skid be located outside the transport reactor development unit (TRDU) gasification tower area. A stand-alone TDA Research data acquisition system was provided as part of the test skid. In addition to the staffing required to operate the necessary gasifier and auxiliaries such as the sulfur reactor, also included as part of the EERC side of the project was the staffing and mercury analyzer necessary to conduct sampling for the Hg. Postrun analysis of the sorbents for trace metal concentrations was the responsibility of TDA.

The first test campaign was conducted taking all of the gas flow from the EERC continuous fluidized-bed reactor (CFBR) while operating on a bituminous coal. A Utah bituminous coal from the Sufco mine was selected as the feedstock for this testing because of its favorable swelling characteristics. The second test campaign was conducted by taking a slipstream test of syngas from the EERC transport reactor while operating on a Texas lignite from the Oak Hill mine near Henderson, Texas. This test was conducted as part of a different lignite gasification project that was also testing sulfur removal, water–gas shifting and hydrogen separation utilizing a hydrogen membrane. TDA Research testing was being piggy-backed on the testing being conducted for the consortium and did not pay for the operation of the TRDU gasifier itself.

TASK 1 – CFBR SYNGAS TESTING ON BITUMINOUS COAL

Equipment Description

Figure 1 shows the 4-lb/hr CFBR used for gasification tests. Figure 2 is a photograph of the fluid-bed reactor system. The unit was originally designed as a pyrolysis unit for a U.S. Department of Energy (DOE) mild gasification program but has since been used for gasification and pyrolysis on a variety of projects. Gases used for fluidization are mixed in a gas manifold. Bottled gases, including hydrogen, house nitrogen, house air, and any liquid desired (such as water), are first preheated, then mixed and heated to temperatures around 400° to 500°C in a superheater (20 ft of ⅜-in. tubing coiled into an 18-in. ceramic fiber heater). Two bottled gases in combination with both house air or house nitrogen and a liquid can be used at the present time. A

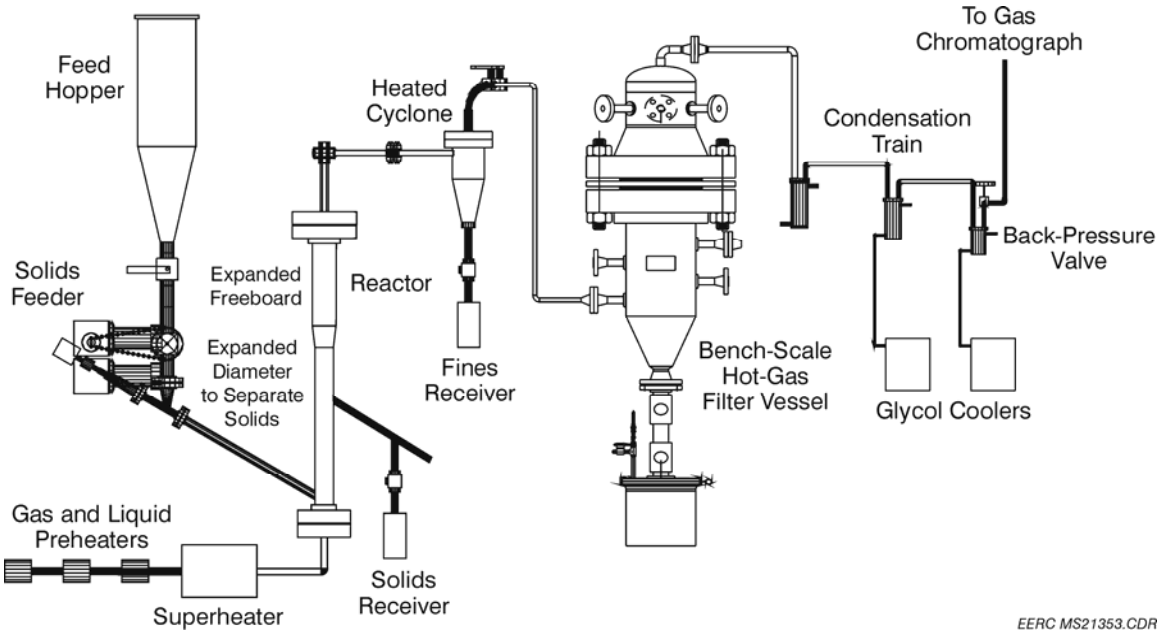


Figure 1. Schematic of CFBR.

Figure 2. Photograph of the 4-lb/hr CFBR.

MAXIMATOR® gas booster is utilized as a recycle syngas compressor to allow syngas to be recycled to the bottom of the gasifier to allow the fluidization velocity to be set independently of the oxidant and steam flow rates without having to dilute the syngas with inert nitrogen.

The reactor is constructed of 316H stainless steel Schedule 80 pipe. The first (bottom) section is made of 3-in. pipe and is 33 in. in length. The next (top) reactor section is made of 4-in. pipe, 18.75 in. in length. The two sections are connected with a 316H weld reducer. The unit was designed such that the top of the fluid bed lies 33 in. above the coal injection point. A solids offtake leg at the top of the bed is the primary means of solids removal from the reactor. A ball valve facilitates collection of the product while the system is operating. The reactor currently has two ceramic fiber heaters to maintain the vessel's temperature and eliminate hot spots. Using external heaters allows the evaluation of internal and external heating methods for process development and scale-up. Current meters were added to the reactor to enable the power consumption of the reactor heaters and the steam superheater to be monitored. The reactor is capable of operation at a maximum of 155 psig and 845°C (1550°F).

A 3-in.-diameter cyclone is used for solids removal from the gas stream. A ball valve allows the changing of the solids catch pot while the system is operating. The cyclone is heated with a ceramic fiber heater capable of operating at a temperature of 900°C (1650°F). Different-sized heated vessels ranging from 2 in. inside diameter (i.d.) to 5 in. i.d. and lengths from 10 in. to 24 in. are available for utilizing various sorbents in a packed-bed mode for conducting contaminate removal (i.e., sulfur, trace metals, etc.) or catalyst testing (i.e., gas shifting). A new circulating fluid-bed reactor for bulk desulfurization has recently been constructed and is currently being integrated with this gasification system. Six 4-in.-diameter vessels are used to remove all condensables from the gas stream. The first condenser pot is indirectly cooled by water and typically cools the gas stream from 300°C (570°F) to 95°C (200°F). The next two condensers, also indirect, are glycol-cooled. The last three are water-cooled. The exit gas temperature is typically 10°C (50°F). A glass wool filter is used to capture aerosols passed through the condenser system.

Not shown in the schematic is a product gas recycle loop. A portion of the gas is taken off between the condensation train and back-pressure control valve, passed through a booster pump to increase the pressure, and fed back to the bottom of the reactor. Using recycled syngas instead of nitrogen as fluidizing gas results in a higher Btu product gas because of the reduction in nitrogen. Recycled syngas is used for pressure tap purges, as well, so that during oxygen-blown operation, the only nitrogen entering the system is from backpulsing the filter vessel and pressuring the coal hopper and cyclone pots during filling and emptying, respectively.

A Genesis software package is used for process control and data acquisition. Two transmitters measure pressure drop across the bed, and thermocouples throughout the unit measure temperature. Temperature and pressure readings are recorded every 30 seconds, and these data are directly transferred to spreadsheets. Online continuous emission monitors for H_2, CO, CH_4, CO_2, and H_2S together with online Foxboro and Yokogawa process gas chromatographs are utilized for measuring gas compositions. If desired, the gas composition of the coal-derived gas stream can be adjusted slightly by adding bottled gas to the gas stream entering the reactor.

Bench-Scale Hot-Gas Filter Vessel (HGFV)

The design and construction of a bench-scale filter vessel that could be used in conjunction with the CFBR (for gasification/pyrolysis) was built to test hot-gas candle filters for their ability to obtain high-temperature, high-pressure operational data on various filter elements. This vessel is designed to handle all of the gas flow from the CFBR at its nominal design conditions. The vessel is 10 in. i.d. and 60 in. long (including cone, vessel, and cap) and can handle a gas flow up to 30 scfm at 843°C (1550°F) and 150 psig. The tube sheet is interchangeable to handle different-sized filters. The filters are sealed in the tube sheet by a bolted metal plate and Nextel™ fiber gaskets which counteract the upward force imparted across the candle filter by the filter's differential pressure. The vessel is sized such that it could handle three candle filters up to 18 in. long with a 2.375-in. outside diameter. This would provide candle space of 3.85 in. centerline to centerline and enable filter face velocities as low as 2.5 ft/min to be tested in the CFBR. Higher face velocities would be achieved by using shorter candles or higher gas flow rates. Ports are added in the filter vessel for allowing temperature and pressure measurements to be obtained. The ash letdown station consists of two high-temperature valves that act as lock hoppers to isolate the ash hopper from the filter vessel.

The nitrogen backpulse system is constructed from existing materials utilized from a previous hot-gas filter test system. The backpulse system is designed to supply a minimum of three candle volumes per pulse for the longest candle filters and even higher volumes for the shorter candle filters. The nitrogen is capable of being heated up to 816°C (1500°F) before entering the filter vessel, although most tests utilize room-temperature nitrogen for backpulsing. The length and volume of nitrogen displaced into the vessel is controlled by the regulated pressure (up to 600 psig) of the cold-nitrogen reservoir and the solenoid valves used to control the timing of the cold-gas pulse, which displaces the hot nitrogen into the filter vessel. An electrically heated ½-in. pipe is used to connect the CFBR to the HGFV.

Sulfur Reactor

The transport reactor for sulfur removal is shown in Figures 3 and 4. Sulfur sorbents are introduced from the feed hopper via a screw feed motor. The sorbents contact the gas stream and are moved upward through the riser and across the top horizontal section. The sorbents and flue gas are then separated in the primary cyclone. The sorbents fall into the standpipe while the syngas exits the top of the reactor and onto the HGFV for fine particulate removal. The sorbents in the standpipe are recycled back to the riser via a second screw feed motor.

Temperature in the system can be adjusted from 300° to 1000°F, allowing for a wide range of testing parameters. Ceramic external heaters are used to maintain run temperature, and multiple thermocouples are used across the system for temperature monitoring. The speed of the recycle screw feeder can be adjusted, which allows for variation of the sorbent recycle rate. Pressure drop is measured in the riser, which allows for calculation of the recycle rate. Standpipe pressure drop is also measured to determine the amount of sorbent accumulated in the standpipe. Nitrogen purges are used to keep the pressure taps free of particulate. Sorbent can be removed

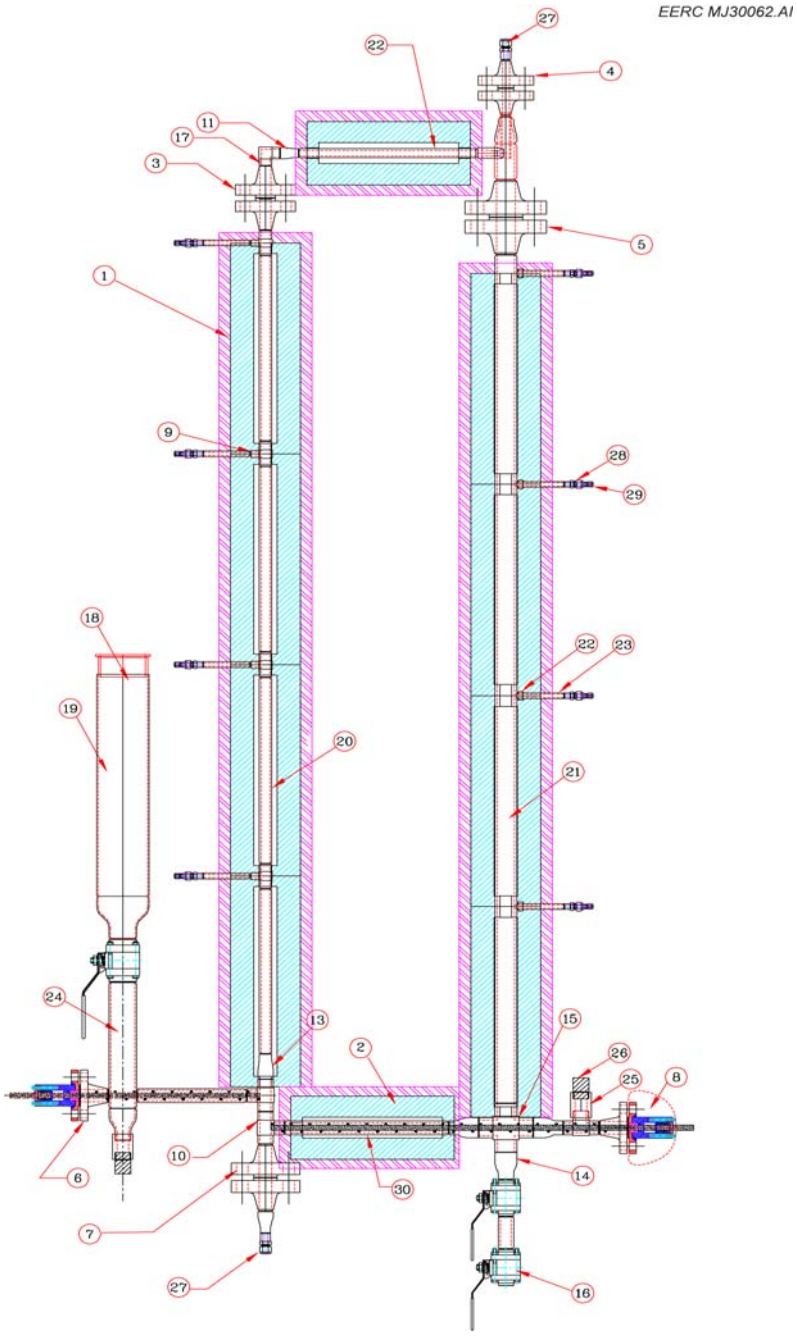


Figure 3. Schematic of the sulfur reactor.

from the system for analysis while testing is in progress via a double-valve hopper system. This also allows for removal of spent sorbent and addition of fresh sorbent while the system is running.

Figure 4. Photograph of the transport reactor for sulfur removal.

RESULTS AND DISCUSSION

Test Plan

The goal of this run was to provide a low-sulfur syngas to be tested using TDA's Hg, As, and Se removal test skid. As such, all tests were performed with the CFBR sending all of its syngas to the sulfur reactor and HGFV before entering the fixed-bed TDA skid. The appropriate H_2S levels had to be achieved before sending syngas to the TDA system. Tests were performed in air-blown mode by mixing oxygen and nitrogen to form an air mixture with a separate recycled syngas stream to provide the remaining gas needed to reach the desired test velocity, in order to provide good flow to the TDA system and to maintain the bed velocity. The test plan was to operate the gasifier at one test condition to provide a consistent syngas composition to the test skid. There were no specific test periods scheduled for this run. However, data reduction and reporting is based on the time periods during which the TDA skid was online and the CFBR was operating at steady state and producing a syngas with the necessary sulfur concentration.

Coal Properties

The proximate–ultimate, x-ray fluorescence (XRF) ash, and heating value analyses for the Sufco coal are shown in Table 1. Table 2 contains the results of a trace metal analysis. The coal

Table 1. Proximate–Ultimate, XRF, and HV for Sufco Coal

Proximate Analysis, wt%	
Moisture	7.3
Volatile Matter	37.0
Fixed Carbon	48.3
Ash	7.4
Ultimate Analysis, wt%	
Hydrogen	5.53
Carbon	67.65
Nitrogen	1.4
Sulfur	0.34
Oxygen	17.68
Ash	7.4
XRF Ash Analysis, wt%	
SiO_2	44.3
Al_2O_3	10.8
Fe_2O_3	5.08
TiO_2	0.84
P_2O_5	0.24
CaO	12.2
MgO	1.85
Na_2O	4.23
K_2O	0.39
SO_3	20.0
Heating Value, Btu/lb	
Calc Calorific Value	11976

Table 2. Trace Metals Analysis of Sufco Coal, µg/g

Arsenic	0.35
Cadmium	0.03
Mercury	0.0381
Selenium	1.25

was sized to -10 mesh and premixed with either a combination of 5% each of dolomite and kaolin or 5% of only dolomite.

Operating Conditions

During testing, the quench pots and cyclone pot were emptied every hour and the filter vessel was backpulsed and emptied periodically as the dP increased. Dräger tube measurements were taken every 1–2 hours at the gas chromatography (GC) and filter vessel to determine H_2S concentration. Sorbent was added to the sulfur reactor periodically to maintain solids inventory

in the system. The finer particles had a tendency to escape the cyclone and end up in the filter vessel ash of the CFBR unit.

After approximately 15 hours of running the CFBR and sulfur reactor in conjunction, steady state and sufficient sulfur removal were achieved. At this time, flow to the TDA system was started. Steady state was maintained for 12 hours before cycling on the TDA skid deadheaded the system causing a major upset. After fixing the problem and again reaching steady state, the TDA system was brought back online for almost 2 hours before agglomeration in bed caused another shutdown. The next steady-state period lasted about 12 hours and was only interrupted by a 30-minute period where the TDA system's program was being updated. This test period again ended because of agglomeration issues in the CFBR. Following maintenance on the CFBR unit, steady state was achieved for over 24 hours, ending when the sulfur reactor auger failed. However, this period was broken up into three tests because of adjustments to steam flow rate. Following repair of the auger, the unit was started up again, and the last test period lasted just under 4 hours.

As was stated earlier, the original plan was to use recycled syngas along with supplemental nitrogen, but resulting from some problems with the recycle gas booster, recycle syngas gas was off-line for a good portion of the run. In order to compensate for the lost gas velocity, nitrogen flow was increased, thus diluting the product gas; however, the net feed rate of the trace metals coming in with the coal remained approximately the same.

Results

The CFBR includes a data acquisition and control system that saves operating data every 30 seconds. These data include reactor temperatures; steam, air, oxygen and nitrogen flow rates; calculated fluidizing velocity; differential pressure across the bed; differential pressure across the filter vessel; and product gas composition. Table 3 shows the main steady-state operating conditions in the CFBR during each test period.

The product gas composition was measured using a Yokogawa gas chromatograph, sampling and analyzing a point sample of gas every 10 minutes. A steady-state test period begins when the gas composition has lined out. Table 4 shows the results of the most common components and the corresponding heating value.

As was described earlier, the recycle syngas was off-line for part of the run as indicated by the data presented in Tables 3 and 4. In Table 3, Tests 2–5 show zero recycle gas flow and the increased N_2 flow. Test 6 shows a very low recycle flow because the recycle booster pump was fixed toward the end of this test period and the recycle gas was turned back online. Table 4 shows an increased N_2 concentration during these tests because nitrogen flow was increased to maintain gas velocity in the reactor.

Table 3. Average CFBR Operating Conditions

Test No.	Avg. Bed Temp., °C	Steam Flow, g/hr	N_2 Flow, scfh	Recycle Syngas Flow, scfh	Oxygen Flow, scfh	Coal Feed, lb/hr	Superficial Gas Velocity, ft/s
1	794	923	137.5	250.0	32.0	1.99	0.905
2	803	951	193.2	185.6	28.9	2.06	0.895
3	792	1024	303.7	0.0	25.4	2.72	0.734
4	786	1017	318.1	0.0	25.4	2.50	0.849
5	793	1101	348.1	0.0	26.5	2.12	0.848
6	778	1702	317.3	77.1	28.4	1.80	0.920
7	772	740	108.3	266.1	31.1	2.75	0.856
8	776	936	107.9	263.9	31.1	2.75	0.855

Table 4. Average CFBR Product Gas Composition and Heating Value

Test No.	H_2, %	CH_4, %	CO %	CO_2, %	N_2, %	H_2S, ppm	HV, Btu/scf	N_2-Free HV, Btu/scf
1	6.29	1.40	3.38	6.10	77.16	22.3	45	199
2	4.91	0.56	0.06	2.32	92.22	15.5	22	281
3	7.08	0.75	0.38	2.67	87.49	41.0	32	254
4	6.52	0.64	0.02	2.53	88.68	24.7	28	245
5	5.13	0.52	0.00	2.45	90.53	14.9	22	232
6	5.12	0.54	0.04	3.30	89.85	41.0	22	219
7	5.95	1.46	1.57	7.26	74.51	112.5	39	154
8	9.81	2.06	5.38	6.82	72.31	14.3	70	253

Mercury concentration in the gas leaving the TDA unit was measured via a PSA Sir Galahad continuous emissions monitor (CEM). Table 5 shows the average mercury concentration and the baseline concentrations during each of the test periods. Mercury removal ranged from 80-90% and during the times when the TDA unit was on-line, Hg concentration was below 2 $\mu g/m^3$. Test 3 shows an Hg removal of 100%, but this is most likely inaccurate and is probably due to a problem with the CEM.

Table 6 shows the material balance data from the tests. Some discrepancies in the closure are because of accumulation or entrainment losses from the fluid-bed reactor itself. No solids were added or removed from the bed itself during the testing.

The low-carbon conversions achieved during this testing are primarily the result of low reactivity of the bituminous coal as compared to the more reactive low-rank coals typically tested, where 85% to 95% carbon conversion is more typical even when operating at the 1550°F maximum operating temperature. Higher-temperature operation, if it were possible in the CFBR, would result in better carbon conversion.

Table 5. Average Mercury Removal per Test Period

Test No.	Hg Baseline, μg/m^3	Hg Concentration, μg/m^3	% Hg Removal
1	7.10	0.67	90.56
2	7.21	1.08	85.02
3	9.55	0.00	100.00
4	8.47	1.24	85.36
5	8.47	1.36	83.94
6	8.47	1.34	84.18
7	8.47	1.63	80.76
8	NA	NA	NA

Table 6. CFBR and Sulfur Reactor Material Balance

Test No.	Coal Feed, lb/hr	Sulfur Sorbent, g/hr	Steam Flow, g/hr	Cyclone, g/hr	Cyclone LOI,[1] %	FV,[2] g/hr	FV LOI, %	Quench Pots, g/hr	Solid and Liquid Closure %	Solids CC, %
1	1.99	45	923	311	62.1	463	1.01	1024	101.3	71.6
2	2.06	47	951	474	70.8	411	1.01	775	90.6	52.9
3	2.72	62	1024	338	71.4	140	5.2	832	59.9	73.9
4	2.5	57	1017	507	62.3	140	5.2	889	73.6	63.1
5	2.12	48	1101	241	60.5	195	2.8	995	71.3	79.6
6	1.81	41	1702	273	60.5	262	2.8	1360	76.5	72.8
7	2.75	62	740	400	60.5	249	2.8	1203	96.7	74.1
8	2.75	62	936	499	78	450	18.6	1073	95.7	50.9

[1] Loss on ignition.
[2] Filter vessel.

TASK 2 – TRDU SLIPSTREAM TESTING WITH THE TDA RESEARCH TEST SKID

Equipment Description

The pilot-scale TRDU has an exit gas temperature of up to 980°C (1800°F), a gas flow rate of 325 scfm (0.153 m^3/s), and an operating pressure of 120 psig (9.3 bar). The TRDU system can be divided into three sections: the coal feed section, the TRDU, and the product recovery section. The TRDU proper, as shown in Figure 5, consists of a riser reactor with an expanded mixing zone at the bottom, a disengager, and a primary cyclone and standpipe. The standpipe is connected to the mixing section of the riser by an L-valve transfer line. All of the components in the system are refractory-lined and designed mechanically for 150 psig (11.4 bar) and an internal temperature of 1090°C (2000°F). Detailed design criteria and a comparison to actual operating conditions on the design coal are given in Table 7.

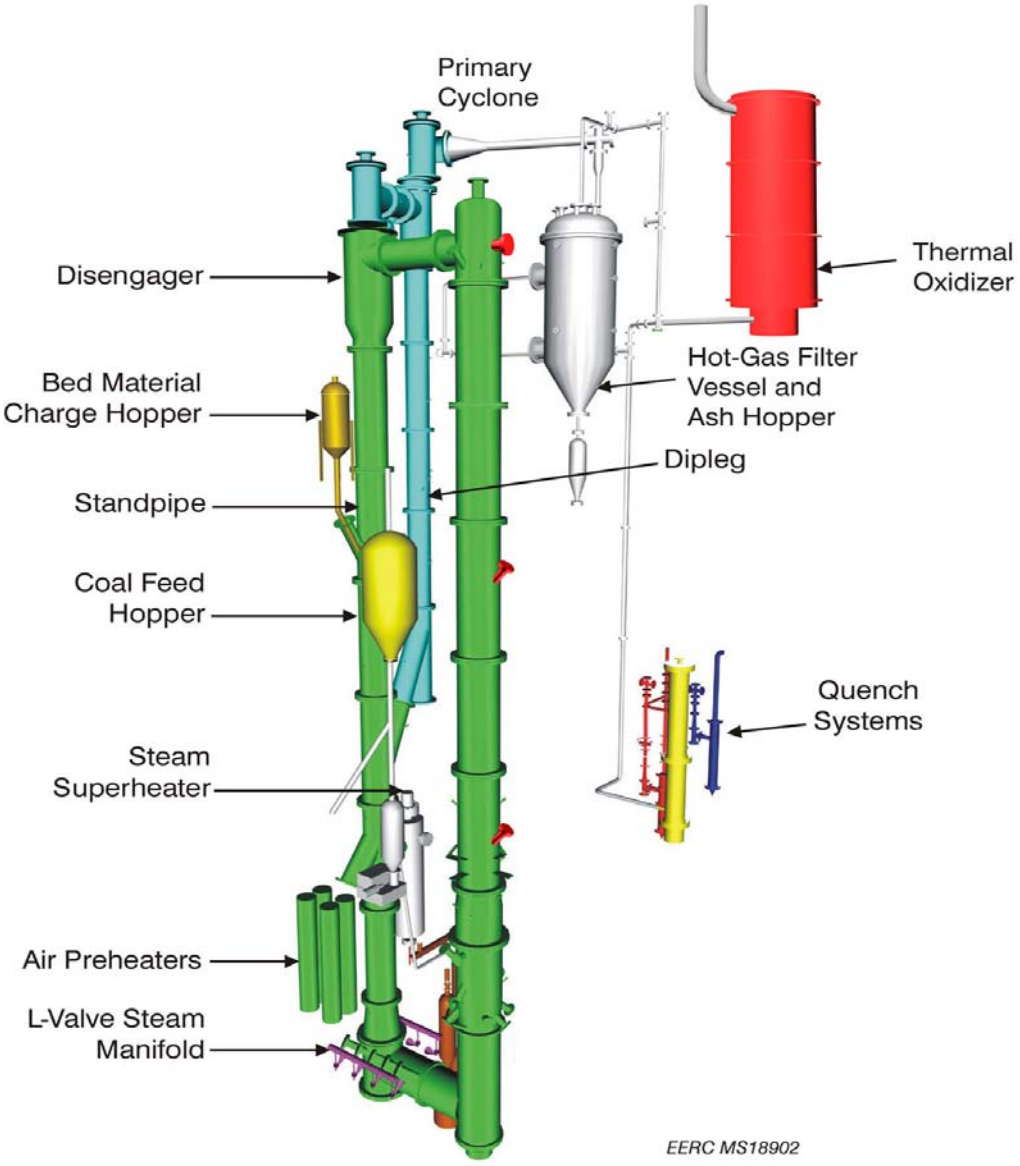


Figure 5. TRDU, HGFV and thermal oxidizer in the EERC gasification tower.

The feedstock fed to the transport reactor can be admitted through three nozzles, which are at varying elevations. Two of these nozzles are located near the top of the mixing zone (gasification mode), and the remaining one is near the bottom of the mixing zone (combustion mode). During operation of the TRDU, feed is admitted through only one nozzle at a time. The feed is fed by a revolutions-per-minute (rpm)-controlled metering auger and monitored by the coal addition rates to the pressurized feed hoppers. Oxidant is fed to the reactor through two pairs of nozzles at varying elevations within the mixing zone.

Table 7. Summary of TRDU Design and Operation on the Design Coal

Parameter	Design[1]	Actual
Coal	Illinois No. 6	Illinois No. 6
Moisture Content, %	5	8.5
Pressure, psig	120 (9.3 bar)	120 (9.3 bar)
Steam/Coal Ratio	0.34	0.34
Air/Coal Ratio	4	2.3
Ca/S Ratio, mole	1.5	2
Air Inlet Temperature, °C	427	380
Steam Preheat, °C	537	350
Coal Feed Rate, lb/hr	198 (89.9 kg/hr)	220 (99.9 kg/hr)
Gasifier Temperature, maximum °C	1010	950
ΔT, maximum °C	17	60 to 100
Carbon Conversion,[2] %	> 80	76.5
HHV[3] of Fuel Gas, Btu/scf (cor.[4])	100	110
Heat Loss as Coal Feed, %	19.5	13[5]
Riser Velocity, ft/s	31.3	25
Heat Loss, Btu/hr	252,000	450,000[5]
Standpipe Superficial Velocity, ft/s	0.1	0.38

[1] Kellogg, Brown, and Root (KBR) design specifications.

[2] Carbon conversion = (wt carbon feed − wt carbon removed)/wt carbon feed × 100.

[3] Higher heating value.

[4] Corrected.

[5] Higher coal feed rate and lower air and steam preheat resulted in lower percent heat loss but higher net heat loss.

For the combustion mode of operation, additional nozzles are provided in the riser for feeding secondary air. Hot solids from the standpipe are circulated into the mixing zone, where they come into contact with the air/nitrogen and the steam being injected into the L-valve loop seal. This feature enables spent char to contact steam and oxygen prior to the fresh coal feed. This staged gasification process enhances process efficiency. Gasification or combustion and desulfurization reactions are carried out in the riser as coal/biomass, sorbent, and oxidant (with steam for gasification) flow up the reactor. The solids circulation into the mixing zone is controlled by fluffing gas in the standpipe, L-valve aeration flows, and the solids level in the standpipe.

The riser, disengager, standpipe, and cyclones are equipped with several internal and skin thermocouples. Nitrogen-purged pressure taps are also provided to record differential pressure across the riser, disengager, and cyclones. The data acquisition and control system scans the data points every 0.5 s and saves the process data every 30 s. The bulk of entrained solids leaving the riser is separated from the gas stream in the disengager and circulated back to the riser via the standpipe. A solids stream is withdrawn from the standpipe via an auger to maintain the system's solids inventory. Gas exiting the disengager enters a primary cyclone. Gas exiting this cyclone enters a series of jacketed-pipe heat exchangers before entering the HGFV. The cleaned syngas leaving the HGFV is depressurized and combusted in a thermal oxidizer. Heat and material balance data from around the thermal oxidizer provide an additional measure of carbon

conversion and sulfur removal. Even with the large amount of nitrogen purges and relatively high heat losses, the fuel gas from the TRDU is of generally sufficient quality to sustain combustion in the thermal oxidizer without the requirement of supplemental fuel.

HGFV

This vessel is designed to handle all of the gas flow from the TRDU at its expected operating conditions. The vessel is approximately 48-in. i.d. (121.9 cm) and 185 in. (470 cm) long and is designed to handle gas flows of approximately 325 scfm at temperatures up to 815°C (1500°F) and pressures of 120 psig (8.3 bar). The refractory has a 28-in. (71.1-cm) i.d. with a shroud diameter of approximately 22 in. (55.9 cm). The vessel is sized such that it could handle candle filters up to 2.0 m long; however, 1.5-m iron aluminide metal candle filters were utilized in these reported gasification tests. Candle filters are 2.375 in. (6 cm) o.d. with a 4-in. (10.2-cm) centerline-to-centerline spacing. The filter design criteria are summarized in Table 8. A schematic of the filter system is shown in Figure 6.

The total number of candles that can be mounted in the current geometry of the HGFV tube sheet is 19. This enables filter face velocities as low as 2.0 ft/min to be tested using 1.5-m candles. Higher face velocities are achieved by using fewer candles. The majority of testing has been performed at a face velocity of approximately 4.0 to 4.5 ft/min. These recent tests have utilized the sintered metal (iron aluminide) and Vitropore silicon carbon ceramic candles from Pall Advanced Separation Systems Corporation.

The ash letdown system consists of two sets of alternating high-temperature valves with a conical pressure vessel to act as a lock hopper. Additionally, a preheat natural gas burner attached to a lower inlet nozzle on the filter vessel can be used to preheat the filter vessel separately from the TRDU. The hot gas from the burner enters the vessel via a nozzle inlet separate from the dirty gas.

Table 8. Design Criteria and Actual Operating Conditions for the Pilot-Scale HGFV

Operating Conditions	Design	Actual
Inlet Gas Temperature	540°C	260°–580°C
Operating Pressure	150 psig (10.3 bar)	120 psig (8.3 bar)
Volumetric Gas Flow	325 scfm (0.153 m^3/s)	350 scfm (0.165 m^3/s)
Number of Candles	19 (1 or 1.5 m)	13 (1 m)
Candle Spacing	4 in. ℄ to ℄ (10.2 cm)	4 in. ℄ to ℄ (10.2 cm)
Filter Face Velocity	2.5–10 ft/min, (1.3 to 2.3 cm/s)	4.5 ft/min, (2.3 cm/s)
Particulate Loading	<10,000 ppmw	<38,000 ppmw
Temperature Drop Across HGFV	<30°C	25°C
Nitrogen Backpulse System Pressure	up to 600 psig (42 bar)	250 to 350 psig (17 to 24 bar)
Backpulse Valve Open Duration	up to 1 s	½ s

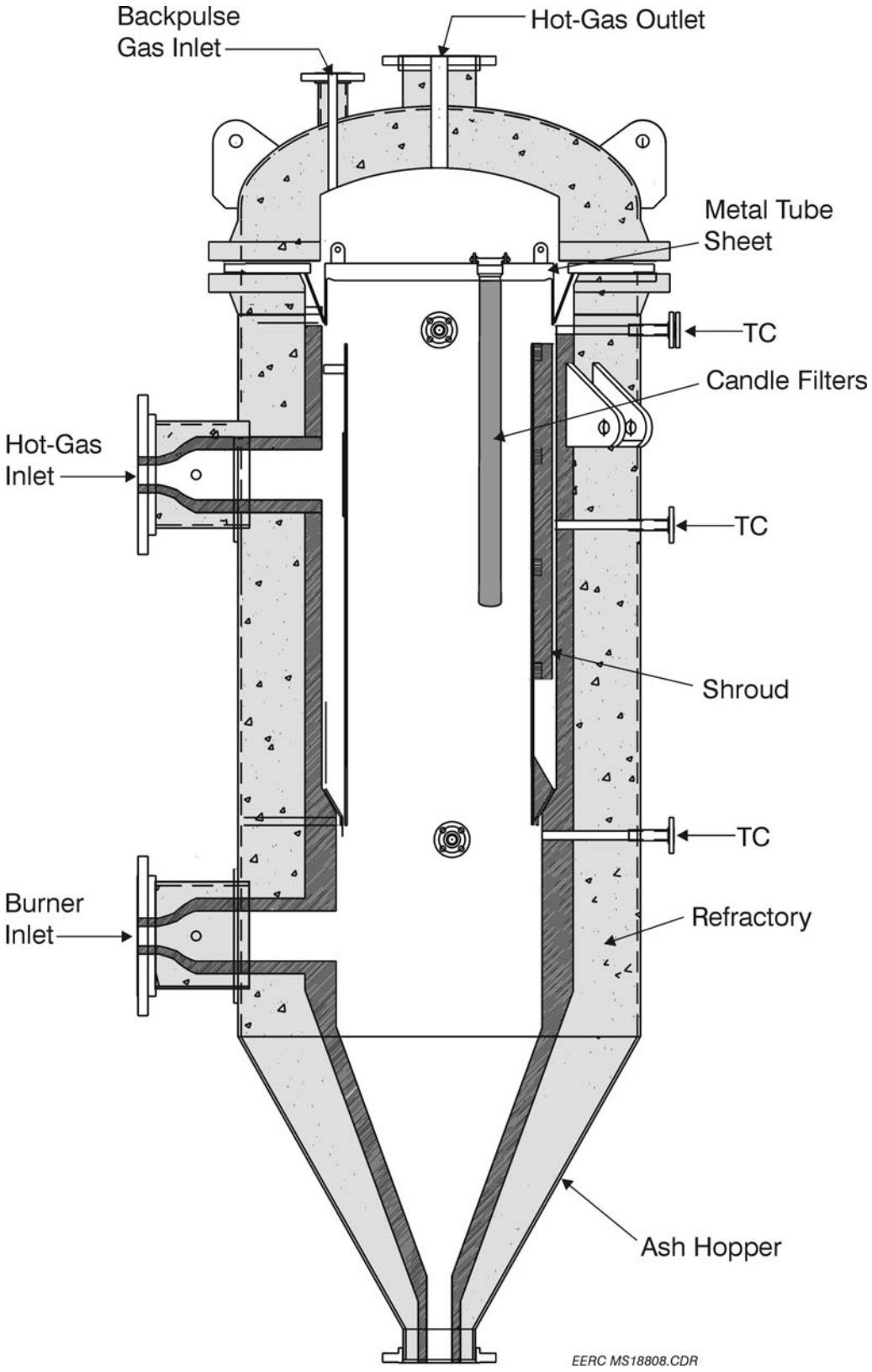


Figure 6. Schematic of filter vessel design with internal refractory, tube sheet, and shroud.

The high-pressure nitrogen backpulse system is capable of backpulsing up to four sets of four or five candle filters with ambient-temperature nitrogen in a time-controlled sequence. The pulse length and volume of nitrogen displaced into the filter vessel are controlled by regulating the pressure (up to 600 psig [42 bar]) of the nitrogen reservoir and controlling the solenoid valve pulse duration. Figure 5 also shows the filter vessel location and process piping in the EERC gasifier tower. Lower operating filter temperatures around 260°C (500°F) were tested utilizing recent modifications that added extra heat exchange surface in order to operate the filter vessel at these lower temperatures. Most of the previous filter tests were completed in the 425°–650°C (800°–1200°F) range. Ports for obtaining hot, high-pressure particulate and trace metal samples both upstream and downstream of the filter vessel are part of the filter system piping.

This testing sent a slipstream of TRDU fuel gas that had been filtered in the pilot-scale HGFV through a heat-traced line directly to the bench-scale transport desulfurizer, the bench-scale filter vessel, and the quench system discussed previously before being depressurized and the flow rate measured.

RESULTS AND DISCUSSION

Test Plan

The goal of this run was to provide a syngas slipstream from the TRDU to the CFBR process area where several warm-gas cleanup technologies will be tested, including the transport reactor for sulfur removal and TDA's skid for mercury and trace element control. The process schematic is shown in Figure 7. All warm-gas cleanup procedures were performed at temperatures over 400°F. Table 9 shows the planned test schedule for the TRDU. Flow was opened to the warm-gas cleanup units once a baseline steady state on the TRDU was reached. Each unit in Figure 7 was brought online one at a time to determine a new baseline for each step in the process train. As was done during the CFBR syngas run, gas was not allowed to flow through the TDA system until sulfur removal in the transport reactor desulfurizer was sufficient.

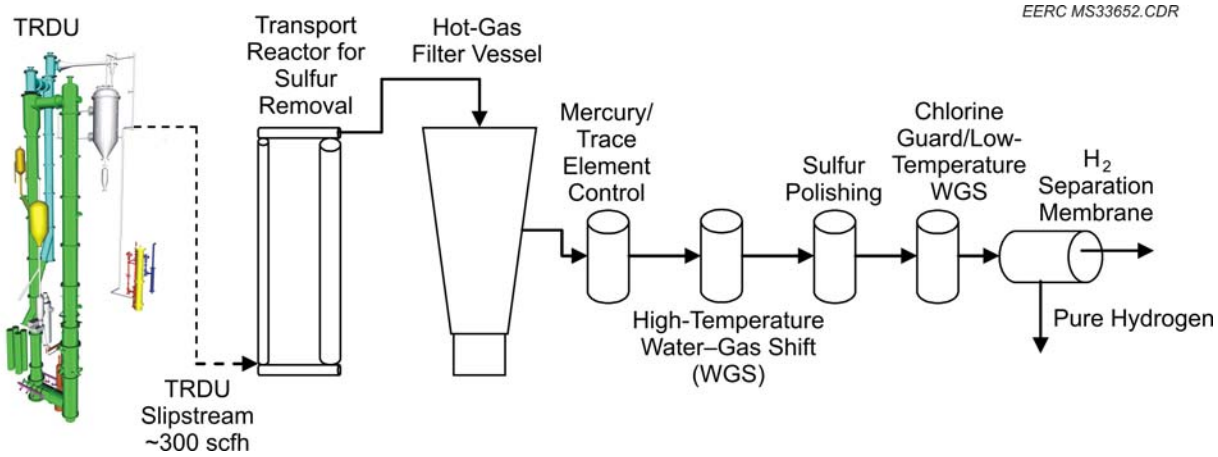


Figure 7. Process schematic for the TRDU slipstream warm-gas cleanup.

Table 9. TRDU Test Plan

Test No.	Coal	Coal Feed, lb/hr	Temp, °C	Oxidant
1	As Received	400	840	Air
2	As Received	450	840	Air
3	As Received	500	840	Air
4	As Received	500	870	Air
5	As Received	450	870	Air
6	As Received	400	870	Air
7	As Received	350	870	Air
8	Air Dried	350	900	Air
9	Air Dried	400	900	Air
10	Air Dried	400	870	O_2
11	Air Dried	450	900	O_2
12	Air Dried	350	900	O_2
13	Air Dried	400	900	O_2
14	Air Dried	450	870	O_2
15	Air Dried	450	930	O_2
16	Air Dried	400	930	O_2

Fuel Analysis

Proximate–ultimate, XRF analysis (XRFA), and heating value analyses for the Oak Hill lignite coal used during this run are located in Table 10. Particle-size distribution of the coal is shown in Figure 8. The figure shows a d50 of approximately 550 microns. Table 11 contains the trace metal concentrations of interest.

Results

While the TRDU had 16 scheduled test periods, there were only 10 test periods identified on the warm-gas cleanup end of the process, which were divided by changes in the process train flow. Tables 12 and 13 shows the TRDU slipstream composition at the inlets of the sulfur reactor and TDA skid during each of the 10 test periods.

Mercury concentration was analyzed at the outlet of the TDA system via a CEM. Figure 9 depicts a typical mercury concentration versus time data curve taken during Test 6 (longest duration) of the warm-gas cleanup process. This figure shows that while the TDA system was online, Hg concentration was less than 10 $\mu g/m^3$. The figure also shows that when the system was taken off-line, Hg concentration increased dramatically to a baseline of roughly 40–50 $\mu g/m^3$. Table 14 shows the average mercury baseline and concentration during each of the 10 test periods. This data is representative of the time during each test period when the TDA skid was online. The TDA skid was closed to flow during Tests 1, 2, and 7, but during the other test periods, mercury removal ranged from 97.3%–99.9%. Test 9 was lower than this range because the TDA skid was only online for a short time during this period and did not reach steady state before being taken off-line.

Table 10. Proximate–Ultimate, XRFA, and Heating Value for Oak Hill Lignite

	As Received	Air Dried
Proximate Analysis, wt%		
Moisture	32.4	28.6
Volatile Matter	26.2	31.38
Fixed Carbon	31.45	30.96
Ash	9.95	9.07
Ultimate Analysis, wt%		
Hydrogen	6.65	6.44
Carbon	44.07	45.78
Nitrogen	0.95	1.07
Sulfur	0.69	0.72
Oxygen	37.69	36.92
Ash	9.95	9.07
XRF Ash Analysis, wt%		
SiO_2	48.0	48.0
Al_2O_3	23.8	23.8
Fe_2O_3	8.78	8.78
TiO_2	1.12	1.12
P_2O_5	0.16	0.16
CaO	12.8	12.8
MgO	3.77	3.77
Na_2O	0.44	0.44
K_2O	1.12	1.12
SO_3	–	–
Heating Value, Btu/lb	6205	7743

Sampling for arsine and hydrogen selenide was also conducted by TDA personnel during the testing but did not appear to show significant levels with either the inlet or outlet samples. Tables 15 shows that the selenium, arsenic, cadmium, and chlorine seemed to concentrate in the filter ash samples that were collected at approximately 300°C, with very little of these metals remaining in the circulating bed material. Table 16 shows that, although the filter was capable of removing most of the cadmium at an operating temperature of 300°C, significant amounts of arsenic and selenium and all of the mercury were passing through the filter at this temperature. The selenium was predominately being removed by the transport desulfurizer sorbent with only a very small amount being found in the iron-based high-temperature shift located downstream of the TDA skid. Arsenic was not removed by the desulfurization sorbent and ended up downstream of the TDA skid in the iron-based high-temperature shift catalyst, the sulfur polishing sorbent and, to a lesser extent, the low-temperature shift catalyst. Some mercury also reported to the low-temperature shift catalyst. This trace metal penetration is primarily thought to occur when the TDA test skid was off-line; however, only direct analysis of the TDA sorbent will positively determine the sorbent's ability to capture these trace metals.

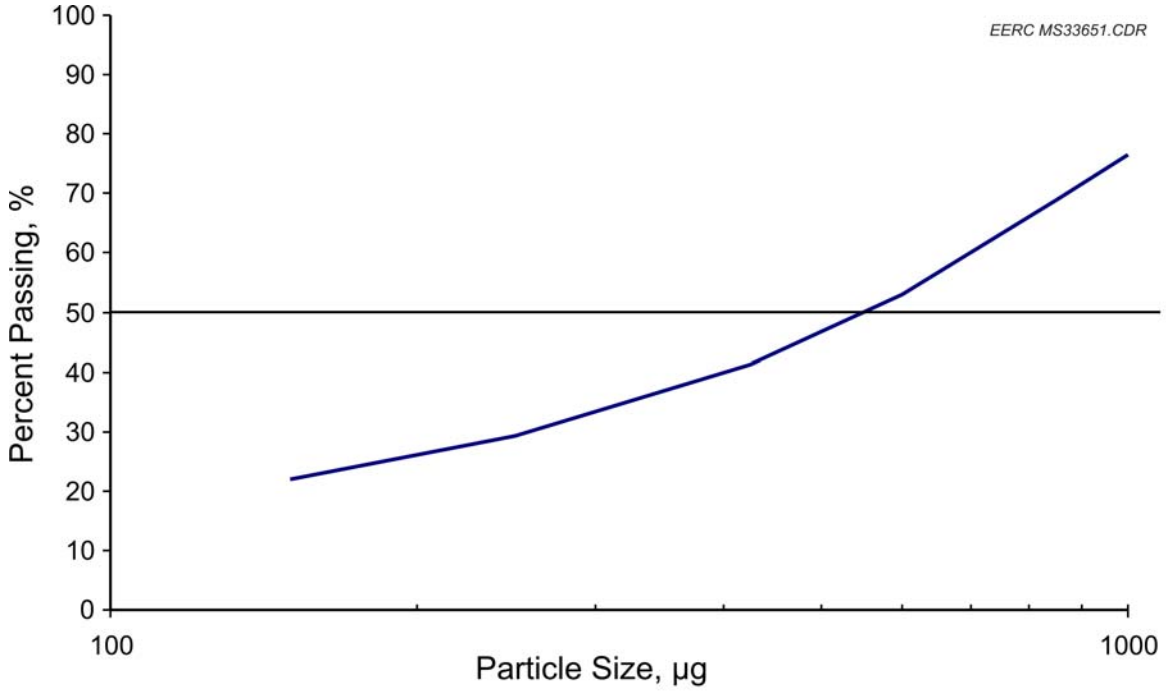


Figure 8. Particle-size distribution of Oak Hill coal.

Table 11. Trace Metal Analysis of Oak Hill Coal

Arsenic	1.27 µg/g
Cadmium	0.20 µg/g
Mercury	0.186 µg/g
Selenium	7.71 µg/g

Table 12. Gas Composition at Inlet of Sulfur Reactor

Test No.	H_2, %	CO, %	CO_2, %	N_2, %	CH_4, %	H_2S, ppm
1	7.06	5.10	15.83	68.28	3.73	3570
2	9.40	5.66	13.66	67.15	1.79	1312
3	8.51	4.86	15.34	69.50	1.74	2947
4	8.87	4.97	15.50	68.25	1.83	1938
5	9.45	5.77	15.37	66.71	1.97	1996
6	9.46	6.61	14.81	66.87	1.75	1906
7	15.38	7.22	21.54	53.37	2.57	2988
8	18.63	7.67	24.71	45.81	3.17	3622
9	17.65	7.57	25.27	46.72	3.00	3330
10	18.88	8.83	25.59	44.70	3.10	3304

Table 13. Gas Composition at Inlet of TDA Skid

Test No.	H_2, %	CO, %	CO_2, %	N_2, %	CH_4, %	H_2S, ppm
1	8.29	4.77	15.03	69.08	1.66	3455.47
2	7.68	4.38	13.83	72.34	1.53	0.59
3	10.89	0.99	16.66	68.58	1.49	0.67
4	11.45	1.00	17.03	67.63	1.61	0.00
5	13.34	0.14	18.41	65.49	1.61	0.00
6	13.69	0.49	19.92	67.23	1.63	0.04
7	17.51	7.95	24.53	55.87	3.09	24.19
8	21.83	1.42	27.91	47.06	2.93	83.89
9	19.72	0.63	27.18	48.95	2.51	0.00
10	20.61	1.41	28.36	47.22	2.68	0.00

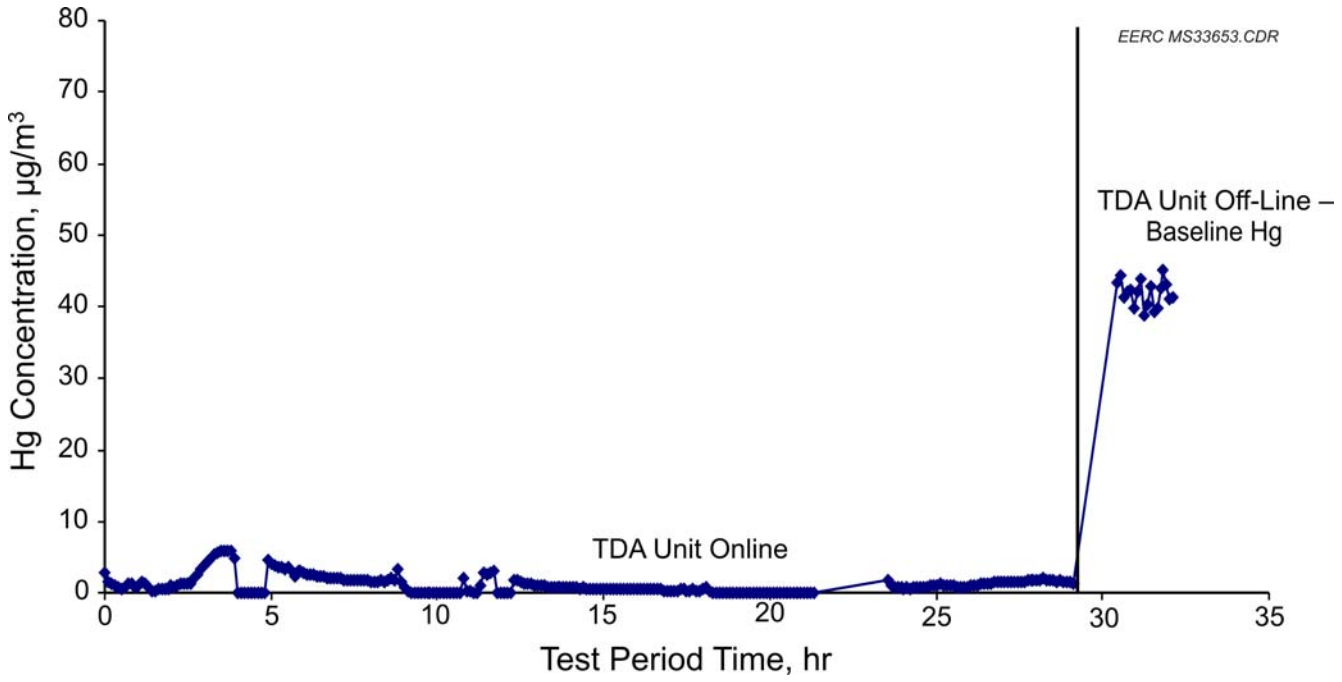


Figure 9. Test 6 CEM mercury concentration data.

Table 14. Average Mercury Removal per Test Period

Test No.	Hg Baseline, μg/m^3	Hg Concentration, μg/m^3	% Removal
1	NA	NA	TDA off-line
2	NA	NA	TDA off-line
3	21.5	0.31	98.56
4	21.5	0.075	99.65
5	21.5	0.018	99.92
6	41.8	1.13	97.30
7	54.7	54.7	TDA off-line
8	56.6	0.108	99.81
9	45.1	6.78	84.97
10	55.8	0.436	99.22

Table 15. Trace Metal Analysis on TRDU Samples

Sample	As, μg/g	Cd, μg/g	Cl, μg/g	Hg, μg/g	Se, μg/g
6/12/08 Coal 0:00–6:00	0.89	0.17	40	0.187	6.83
6/14/08 Coal 0:00–1:00	1.33	0.16	43	0.179	6.72
6/12/08 BM[1] 1:50	0.35	<0.08	11	<0.002	0.87
6/13/08 BM 22:30	<0.2	0.092	13	<0.002	2.73
6/12/08 FV 6:00	7.2	1.3	190	0.002	32.0
6/13/08 FV 22:30	24.6	1.4	237	0.002	26.9
Coal Composite	1.27	0.20	63	0.186	7.71

[1] Bed material.

Table 16. Trace Metal Analysis of Slipstream Samples Around the TDA Test Skid

Sample	As, μg/g	Cd, μg/g	Cl, μg/g	Hg, μg/g	Se, μg/g
Sulfur Reactor	0.69	0.12	–	0.0039	80.6
Filter Vessel	2.92	0.21	–	0.0219	99.4
High-Temp. Catalyst	14.1	<0.2	–	<.001	5.7
Sulfur Polishing Bed	25.1	<0.2	–	<.0009	<0.5
Chlorine Guard Bed	7.89	<0.2	30	1.15	<0.5
Low-Temp. Catalyst	8.53	<0.2	16	1.89	<0.5

CONCLUSIONS

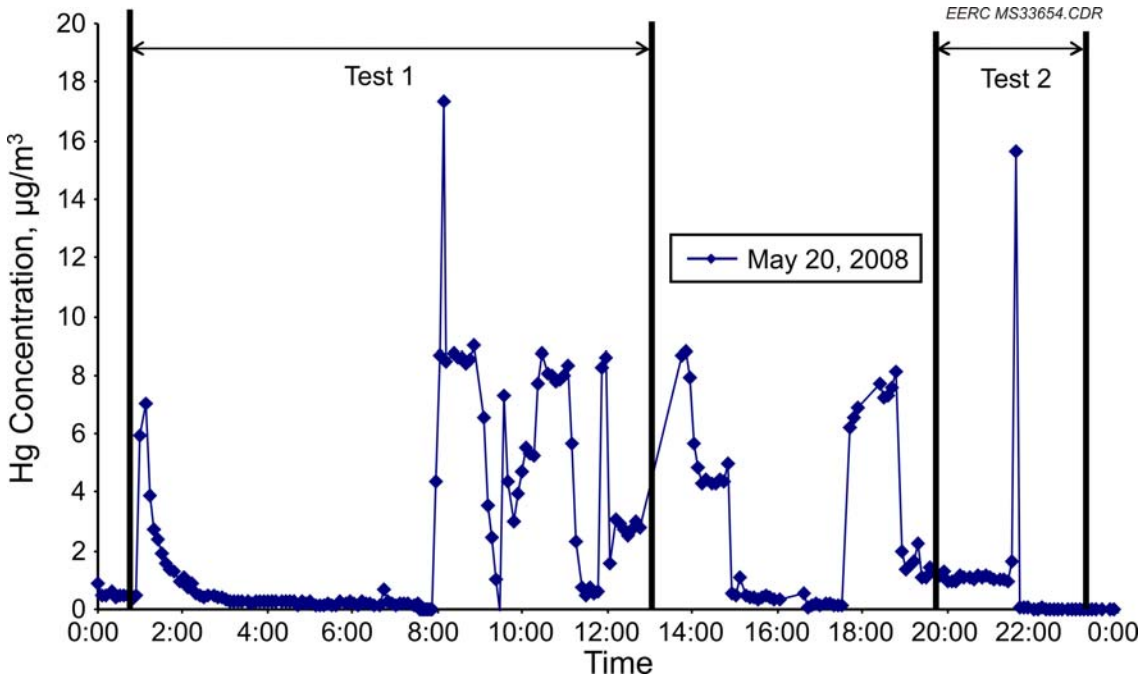
TDA Research, Inc., successfully tested its trace metal sorbent on actual coal-derived syngas from Sufco bituminous coal and on a TRDU slipstream operating on a Texas lignite coal. The EERC also performed independent Hg measurements utilizing a PSA Sir Galahad mercury CEM. The TDA Research sorbent seemed to be very effective for the removal of mercury from the warm syngas. Because of the inability of the hydride analyzer to be able to detect the arsine

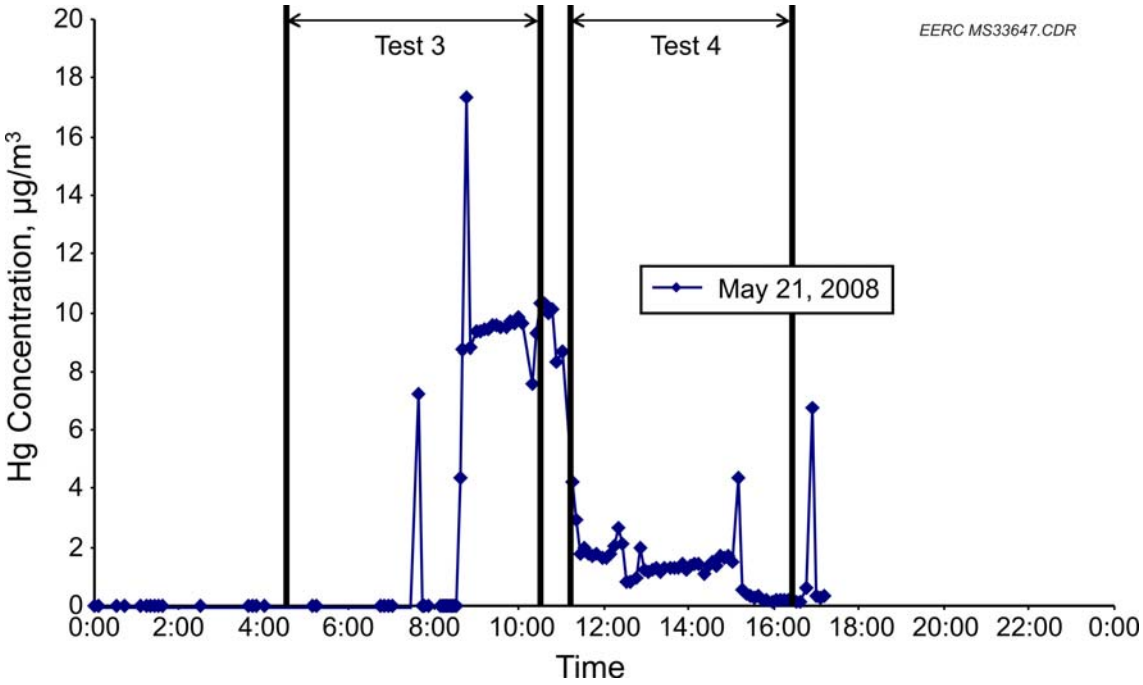
and hydrogen selenide, it was difficult to say whether the sorbent was also effective for these species and analysis of the sorbent by TDA for these trace metals would be necessary. However, since the TDA Research sorbent requires low sulfur concentrations, it does appear that the typical warm-gas sulfur sorbents being tested are going to remove a signficant amount of the hydrogen selenide before it would ever get to the TDA Research, Inc., sorbent.

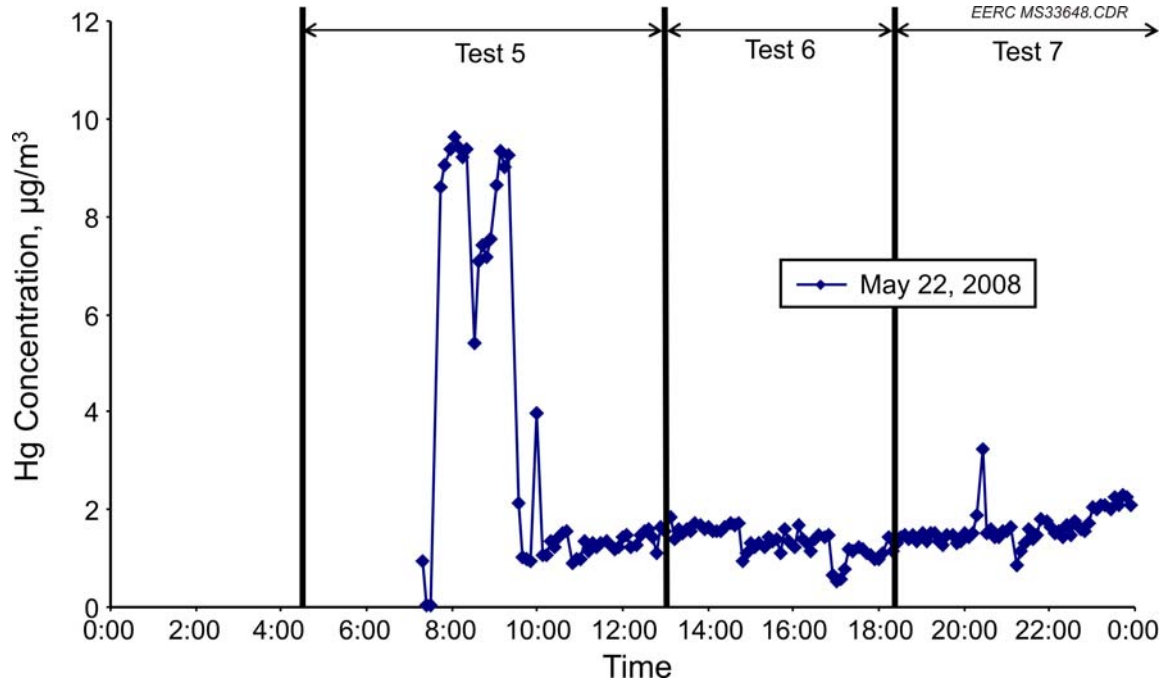
APPENDIX A

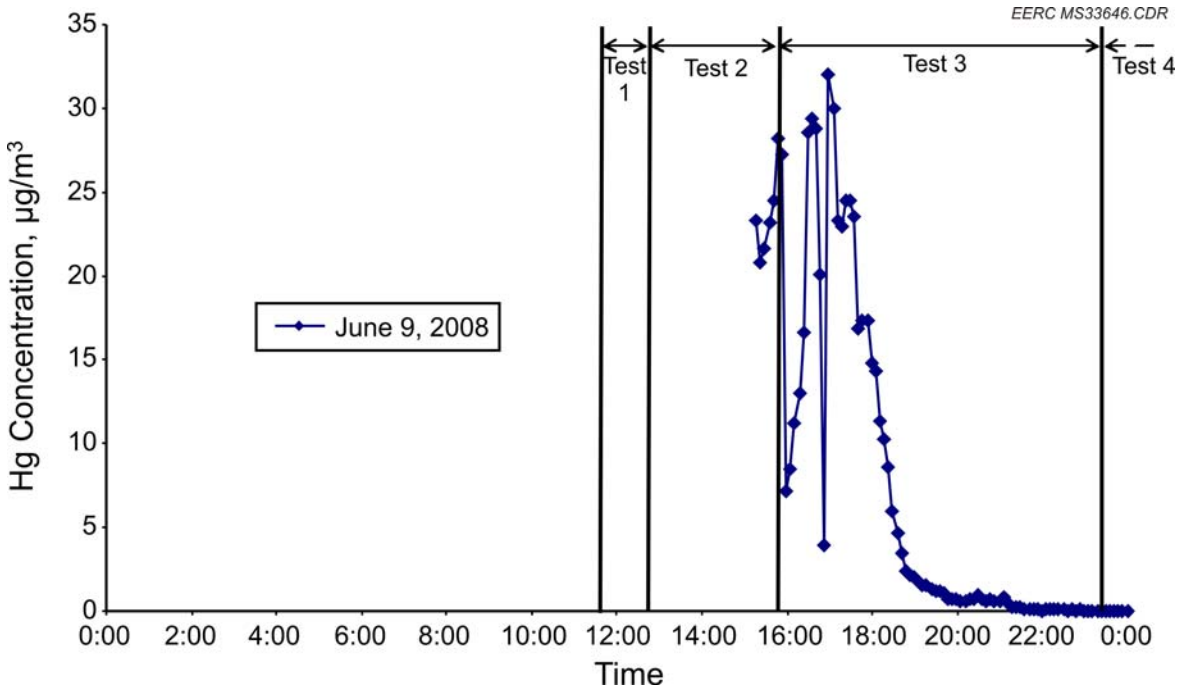
MERCURY CEM CONCENTRATION VERSUS TIME GRAPHS

MERCURY CEM CONCENTRATION VERSUS TIME GRAPHS









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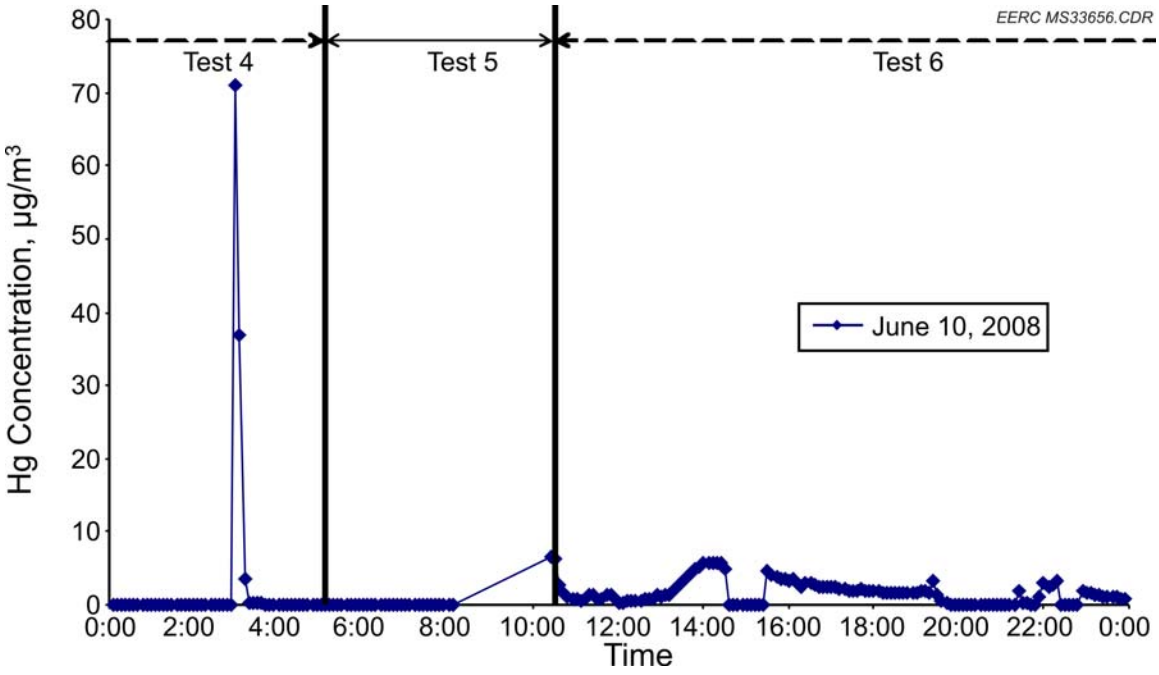
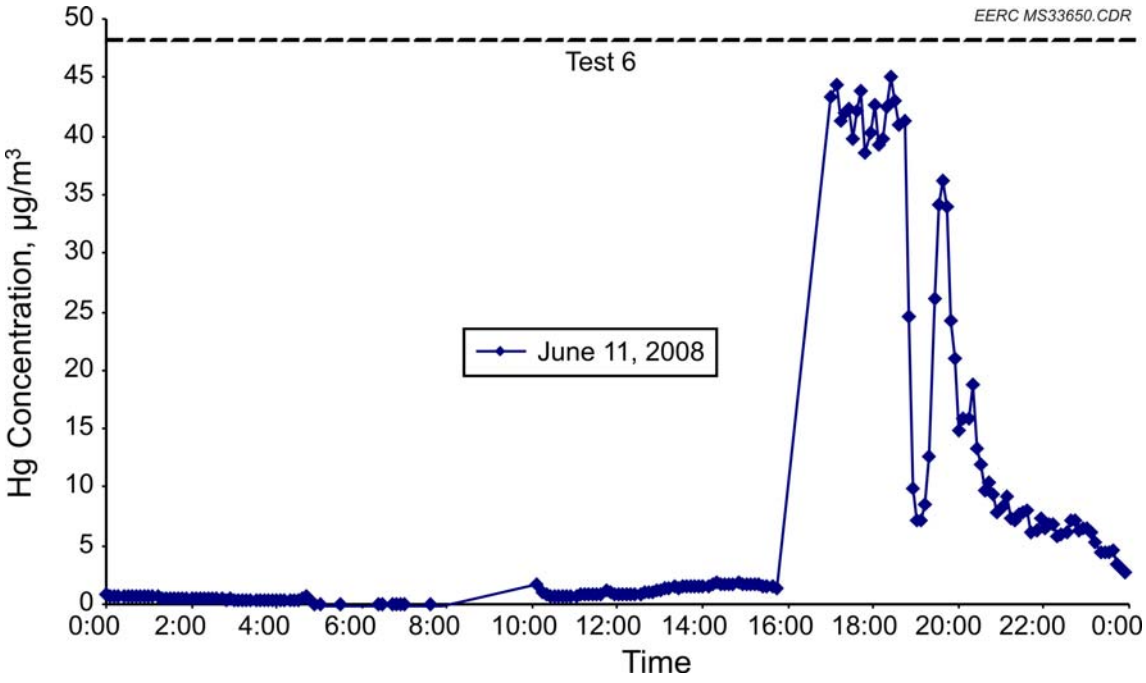

EERC MS33656.CDR
Test 4
Test 5
Test 6
Hg Concentration, µg/m3
June 10, 2008
Time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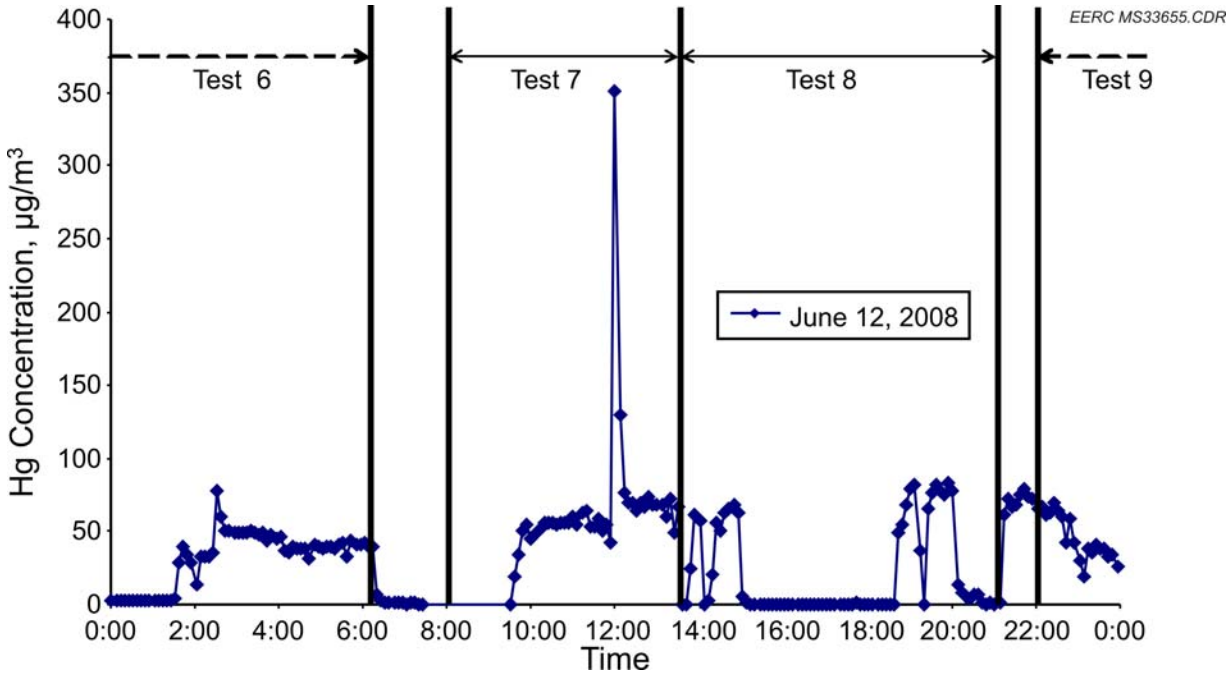
Test 6
Hg Concentration, µg/m3
June 11, 2008
Time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Test 7
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Hg Concentration, µg/m3
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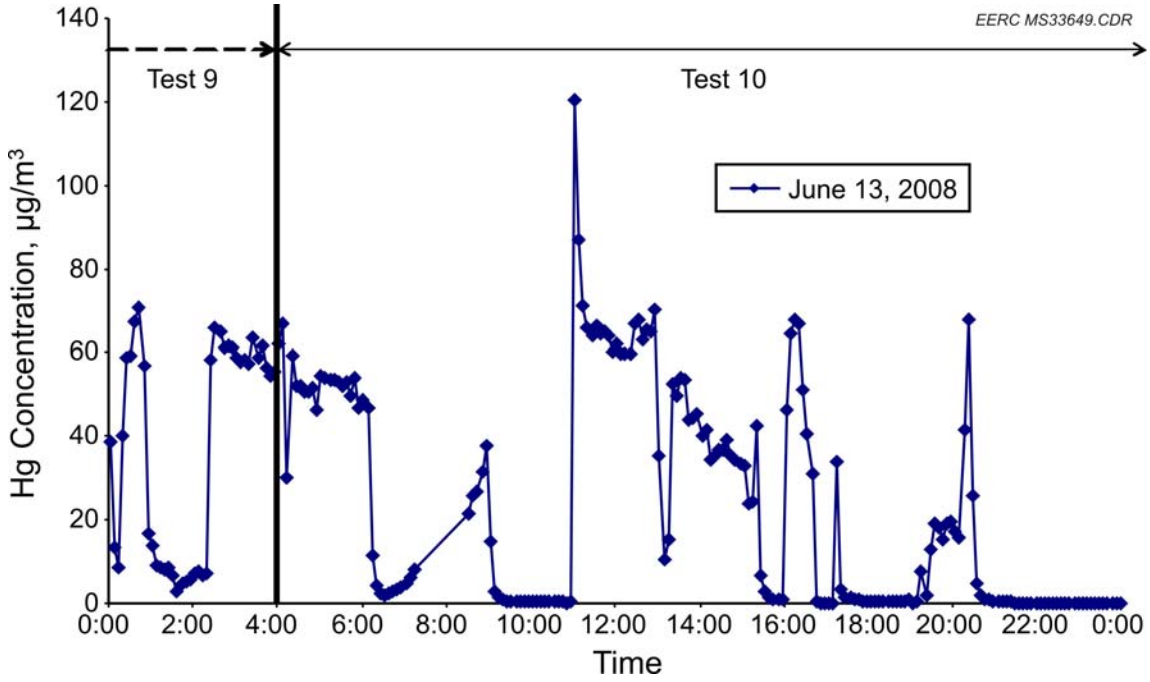
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Test 9
Test 10
Hg Concentration, µg/m3
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5. Appendix B - Power Systems Demonstration Facility

5.1.1 PSDF Facility

The Power Systems Development Facility (PSDF) was established in 1996 to support the Department of Energy's (DOE) effort to develop cost-competitive and environmentally acceptable coal-based power generation technologies (Figure 35). Located near Wilsonville, Alabama, the PSDF was designed at a size that can be reliably scaled up to commercial applications. Development of advanced power systems at the PSDF is focused specifically on identifying ways to reduce capital cost and increase efficiency while meeting strict environmental standards.

Figure 35. Power Systems Demonstration Facility, Wilsonville, Alabama.

The PSDF was conceived as the premier advanced coal power generation R&D facility of the world, serving as the proving ground for many new Advanced Power Systems. Capable of operating at pilot to near-demonstration scales, the facility is large enough to give industry real-life data, yet small enough to be cost effective. The PSDF has developed testing and technology transfer relationships with many vendors to ensure that test results and improvements developed at the PSDF are incorporated into future plants. Major subsystems tested and some highlights of the test program at the PSDF include:

- ***Transport Reactor:*** The Transport Reactor has operated successfully as a pressurized combustor and as a gasifier in both oxygen- and air-blown modes. Several types of coals have been tested in gasification operation including subbituminous, bituminous, and lignite coals. The Transport Gasifier is projected to be the lowest capital cost coal-based power generation option, while providing the lowest cost of electricity and excellent environmental performance.
- ***Advanced Particulate Control:*** Advanced hot gas particulate filtration with more than 30 different filter elements types has been evaluated. Material property testing on filter elements is routinely conducted to assess their suitability for long-term operation. Cooperative work with filter vendors has advanced the technology and aided in identifying commercially suitable materials and designs.
- ***Filter Failsafe Device:*** To enhance filter system reliability and protect downstream components, “failsafe” devices that reliably seal off failed filter elements have been successfully developed.
- ***Coal Feed and Ash Removal Systems:*** Reliable operation of the coal feed system and the ash removal systems had been demonstrated. Modifications developed at the PSDF and shared with the equipment supplier allow current coal feed equipment to perform in a commercially acceptable manner. Innovative, continuous processes for course ash removal from the gasifier and fine ash removal from the particulate filter system were developed at the PSDF and implemented with remarkable results.
- ***Synthesis Gas Cooler:*** A synthesis gas cooler was in place. Material testing has aided in selection of cooler inlet erosion inhibiter material with long-term performance.

- ***Synthesis Gas Cleanup:*** A slipstream synthesis gas cleanup train was constructed and has proven capable of meeting stringent synthesis gas decontamination requirements. This module provides an ultra clean slipstream.
- ***Sensors and Automation:*** Several instrumentation vendors have worked with PSDF personnel to develop and test instruments under process conditions. Automatic temperature control of the Transport Gasifier has been successfully implemented and is now part of routine operation.
- ***Fuel Cell:*** Two 0.5 kW solid oxide fuel cells manufactured by Delphi were successfully operated on synthesis gas from the Transport Gasifier, marking the first time that a solid oxide fuel cell has been operated on coal-derived synthesis gas.
- ***Combustion Turbine Burner:*** Integrating the existing 3.8 MW combustion turbine with a new synthesis gas burner developed by Siemens Power Generation has allowed further system automation and controls development.
- ***Recycle Gas Compressor:*** Stable operation with recycled synthesis gas used for gasifier aeration was successfully demonstrated.

5.1.2 PSDF Gasification Process Description

The PSDF gasification process features high pressure solids feed systems; a KBR (formerly Kellogg Brown & Root) Transport Gasifier; a high pressure filter vessel, the Siemens Westinghouse particulate control device (PCD); continuous ash depressurization systems developed at the PSDF for ash removal; a slipstream synthesis gas cleanup unit to test various pollutant control technologies; and a novel piloted synthesis gas burner (Figure 36). Coal and sorbent (when sulfur capture is required) are separately fed into the gasifier through lock hopper feed systems. Coal is ground to a nominal particle diameter between 250 and 400 microns. Sorbent, either limestone or dolomite, is ground to a nominal particle diameter of 10 to 100 microns. For start-up purposes, a direct propane-fired burner is used for heating the gasifier.

The Transport Gasifier, a pressurized, advanced circulating fluidized-bed reactor, consists of a mixing zone, riser, solids separation unit, seal leg, standpipe, and J-leg. The gasifier is equally capable of using air or oxygen as the gasification oxidant. Steam and either air or oxygen are mixed together and introduced in the lower mixing zone, while the coal, sorbent, and additional air and steam (if needed) are added in the upper mixing zone. These feed streams are mixed together in the upper mixing zone. The gas and solids move up the riser before entering the solids separation unit, which removes larger particles by gravity separation. Between the first and second stages of the solids separation device is the seal leg, which prevents backflow of solids. The solids collected by the solids separation unit are recycled back to the gasifier mixing zone through the standpipe and J-leg. The standpipe level can be reduced by removing solids through the continuous course ash depressurization system. The nominal gasifier operating temperature is 982^{o}C, and the gasifier system is designed to have a maximum operating pressure of 294 psig with a thermal capacity of about 41 million Btu/hr.

The gas exits the Transport Gasifier, passes through the primary gas cooler where the gas temperature is reduced to about 400^{o}C, and enters the PCD for final particulate cleanup. The metal or ceramic filter elements used in the PCD remove essentially all the dust from the gas stream. The PCD utilizes a tube sheet holding up to 91 filter elements, which are attached to one of two plenums. Process gas flows into the PCD through a tangential entrance, around a shroud, and through the filter elements into the plenums. Failsafe devices are located downstream of the filter elements to stop solids leakage by plugging in the event of element

failures. High pressure nitrogen back-pulsing, typically lasting 0.2 seconds, is used to clean the filters periodically to remove the accumulated solids and control the pressure drop across the tube sheet. The solids fall to the bottom of the PCD and are removed through the continuous fine ash depressurization system.

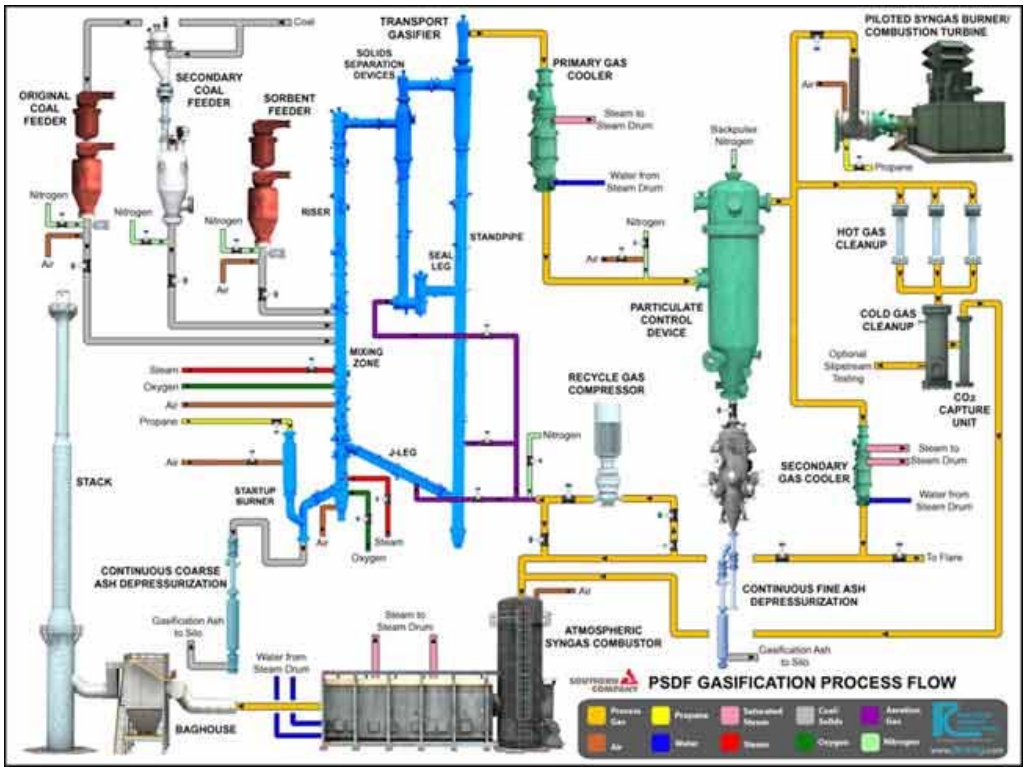

Figure 36. PSDF gasification process.

After exiting the PCD, a portion of the synthesis gas can be directed to the piloted synthesis gas burner (PSB), a gas turbine combustor designed to burn coal-derived synthesis gas with a lower heating value (below 100 Btu/SCF). After combusting in the burner, the gas passes through a turbine before exiting the turbine stack. An associated generator supplies power from the turbine to the electric transmission grid.

A small portion of the synthesis gas, up to 100 lb/hr, can also flow to an advanced gas cleanup system downstream of the PCD. The gas cleanup system is a specialized, flexible unit, capable of operating at a range of temperatures, pressures, and flow rates, and provides a means to test various pollutant control technologies, including removal of sulfur, nitrogen, and chlorine compounds. The synthesis gas cleanup system also includes a CO_2 removal unit. The main stream of synthesis gas is then cooled in a secondary gas cooler, which reduces the temperature to about 450°F. Some of this cooled gas is compressed and sent to the gasifier for aeration to aid in solids circulation. The remaining synthesis gas is reduced to near atmospheric pressure through a pressure control valve. The gas is then sent to the atmospheric synthesis gas combustor which oxidizes carbon monoxide, reduced sulfur compounds (H_2S, COS, and CS_2), and reduced nitrogen compounds (NH_3 and HCN). The gas from the atmospheric synthesis gas combustor goes to a heat recovery boiler, through a bag-house, and then is discharged out a stack.

5.1.2.1 CFBR Equipment Description

Figure 37 shows the 4-lb/hr CFBR used for the gasification of coal and Figure 38 shows a

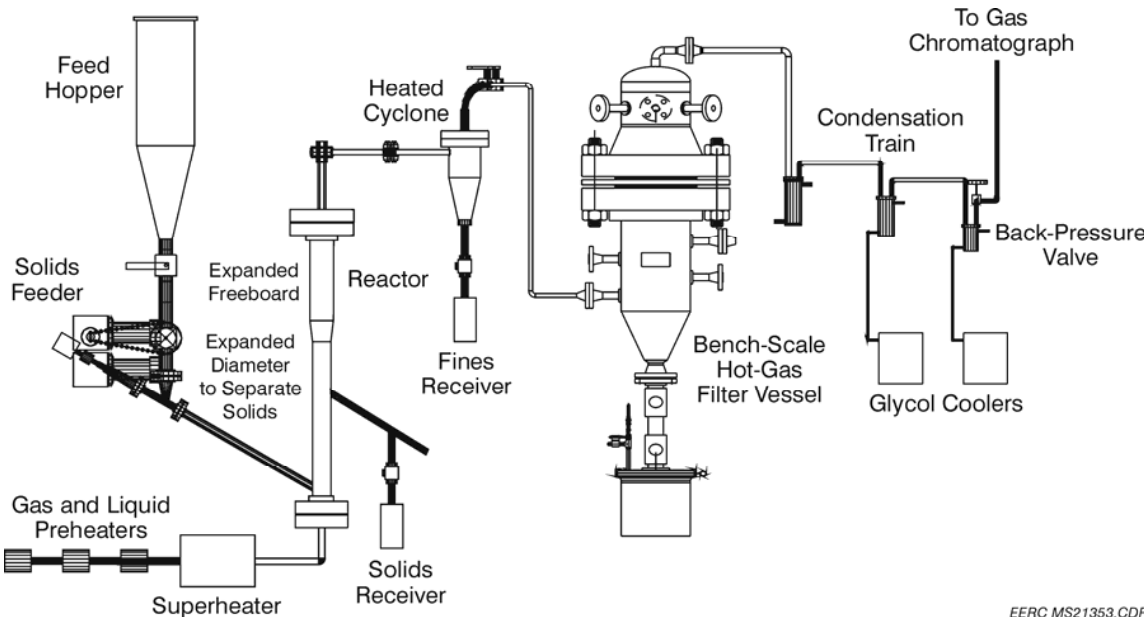

Figure 37. Schematic of UNDEERC's CFBR unit.

photograph of the fluid-bed reactor system. The unit was originally designed as a pyrolysis unit for a DOE mild gasification program but has since been used for various coal gasification and pyrolysis projects. Gases used for fluidization are mixed in a gas manifold. Gases (e.g., hydrogen, oxygen, nitrogen, air) and any liquid (such as water), are first preheated, mixed and then heated to temperatures around 400° to 500°C. A MAXIMATOR® gas booster is utilized as

Figure 38. Photograph of UNDEERC's 4 lb/hr CFBR unit.

a recycle synthesis gas compressor to allow synthesis gas to be recycled to the bottom of the gasifier to allow the fluidization velocity to be set independently of the oxidant and steam flow rates without having to dilute the synthesis gas with inert nitrogen.

The reactor is constructed of 316H stainless steel Schedule 80 pipe. The first (bottom) section is made of 3-in. pipe and is 33 in. in length. The next (top) reactor section is made of 4-in. pipe, 18.75 in. in length. The two sections are connected with a 316H weld reducer. The unit was designed such that the top of the fluidized-bed lies 33 in. above the coal injection point. A solids off-take leg at the top of the bed is the primary means of solids removal from the reactor. A ball valve facilitates collection of the product while the system is operating. The reactor has two ceramic fiber heaters to maintain the temperature of the vessel and eliminate hot spots. Using external heaters allows the evaluation of internal and external heating methods for process development and scale-up. Current meters were in place to enable the power consumption of the reactor heaters and the steam heater to be monitored. The CFBR is capable of gasifying 4 lb of coal per hour and can operate at a maximum pressure of 155 psig and 845°C (1550°F).

Not shown in the schematic is a product gas recycle loop. A portion of the gas is taken off between the condensation train and back-pressure control valve, passed through a booster pump to increase the pressure, and fed back to the bottom of the reactor. Using recycled synthesis gas instead of nitrogen as fluidizing gas results in a higher Btu product gas because of the reduction in nitrogen. Recycled synthesis gas is used for pressure tap purges, as well, so that during oxygen-blown operation, the only nitrogen entering the system is from back-pulsing the filter vessel and pressuring the coal hopper and cyclone pots during filling and emptying, respectively. A Genesis software package is used for process control and data acquisition. Two transmitters measure the pressure drop across the bed, and thermocouples throughout the unit measure temperature. Temperature and pressure readings are recorded every 30 seconds, and these data are directly transferred to spreadsheets. Online continuous emission monitors for H_2, CO, CH_4, CO_2, and H_2S together with online Foxboro and Yokogawa process gas chromatographs are utilized for measuring gas compositions. If desired, the gas composition of the coal-derived synthesis gas stream can be adjusted slightly by adding bottled gas to the stream entering the reactor.

6. Appendix C: Preliminary Cost Analysis

6.1 System Analysis and Cost Assessment

Based upon the experimental results, we carried out a preliminary system analysis in which we sized all major process equipment and estimated costs. In this preliminary assessment, we used the following approach:

1) Select a basis of operation
2) Design the system for Hg removal since its removal determines the size of sorbent inventory
3) Carry out mass and heat balances across each unit given in the process schematic
4) Estimate the size and installed costs of major components
5) Estimate the annual operating and maintenance costs
6) Using a capital recovery cost and annual operating and management (O&M) costs, calculate the cost of removal of mercury on a unit mass basis

6.2 Identification of Basis of Operation

We initiated the cost analysis work by first identifying the plant size. In current industrial practice, IGCC power plants tend to be very large as they greatly benefit from the economies of scale (the cost of electricity goes down as the capital cost per MW decreases). In this analysis, we used the framework of a previous assessment provided by Rutkowski and coworkers (their results are presented in the Gasification Technology Meeting, 2002). In their study, they assessed the economic potential of using an expendable sulfur impregnated activated carbon sorbent to remove mercury from coal-derived synthesis gas at *ambient* temperature.

Table 17. Plant parameters.

Syngas, kmol/h	8546
Syngas MW, kg/kmol	21.04
Syngas, kg/h	179808
Temperature, oC	260
Pressure, psia	900
Hg Concentration, ppbw	52
Hg Removed, kg/h	0.0094
Sorbent life, cycles	1
Plant availability	95%
Plant Operation, hr	8322
Cycle Time, h	8322
Mercury loading, kg Hg/kg sorbent	0.0016
Sorbent Requirement, kg/h	6
Sorbent Replacement, kg/year	48632
Syngas, scf/h	6,757,816
Syngas, slh	191381349
Sorbent Density, kg/L	1.02
Sorbent Volume, L	47678
Space Velocity, h-1	4014

In our analysis, we used the same plant parameters as they did to provide a comparison between the high temperature and low temperature mercury removal. The basis of reference is the Clean Coal Technology Demonstration Plant at Polk County, Florida. This is a 250 MWe IGCC power plant with the operation parameters provided in Table 17. Although we believe that all the new coal-to-chemicals and advanced power generation systems will be in much larger size to benefit from economies of scale, we used the size of the Polk County plant as a basis to have a comparison of the cost of mercury removal between the TDA technology and a low temperature adsorption based Hg removal technology.

The average concentration of mercury in the coal used in that particular plant location is estimated as 100 ppb on weight basis. After the gasification step, this is diluted to 52 ppbw. Using 90% mercury removal as a criterion, we allowed for 5.0 ppbw mercury to leave the sorbent bed at breakthrough. We used the same plant capacity factor (80%) and estimated 130.5 lbs of mercury to be removed on an annual basis.

Chemical process engineering approaches were used for flow sheet development and analysis. First, we carried a mass balance based on total gas flows for each process stream. After completing the mass balance we carried the energy balance across the units based upon the inlet and exit temperatures of each stream.

Based upon the mass and heat transfer calculations carried across each unit, we calculated the cost of major process equipments. In the costing the units, we followed the procedures provided by Association for Advancement of Cost Engineering (AACE) for a Level 5 cost analysis. Level 5 analysis, although limited in scope, provides a good understanding of the economic feasibility of the system on a preliminary basis. Level 5 analysis is widely accepted as a reasonable indicator for showing whether the concept has merits deserving a more detailed analysis. The first step in calculating the direct costs was to size the major equipment items and formulate the bare equipment costs (manufactured selling costs). The bare equipment costs are determined using cost curves, and consulting size/cost charts. Vendor costs were not obtained. We then included a factored estimating methodology to build upon the bare equipment costs. These factors determined the amount of labor to set the equipment, distributive or bulk material and labor costs for buildings, foundation, piping electrical and instrumentation costs.

Before starting cost analysis, we first established the basis for selecting the construction materials. Table 18 presents the criteria of material of selection as a function of upper temperature and pressure limits. We then calculated the size of each instrument to be used in the bare cost equipment analysis.

Table 18. Criteria for material selection as a function of upper temperature and pressure limits

Material	Upper Temperature Limit (°C)	Upper Pressure Limit (psia)
Inconel	<815	<150
Stainless Steel 316	815	150
Stainless Steel 304	650	150
Carbon Steel A285	480	150
Carbon Steel A205	260	150

6.3 Reactor Size and Cost

We carried out a preliminary conceptual design of the reactors that will house the sorbent to control mercury and other trace metal contaminants. We estimated the size of the sorbent reactors based upon sorbent performance and absorption capacity at a gas/solid contact time 0.072 sec at STP (i.e., ~2.0 sec at the empty reactor volume-based residence time at process conditions).

To estimate the size of the reactors we used the specifications provided by “Chemical Plant Design and Economics Handbook” by Peters and Timmerhaus (1982). We designed the both high temperature and low temperature sorbent beds as semi moving-bed reactors using identical designs. These reactors are externally insulated to maintain desired operating temperatures with minimum heat leakage. Based upon the upper temperature and pressure limits given in Table 18, we selected Carbon Steel A285 for the construction material. The required dimensions, thickness and weight of each component used in the design of the

moving-bed reactors are given in Table 19. We then calculated the bare equipment cost based upon material and used a factor for labor and installation reflecting 2002 dollar values.

We calculated the costs for the reactor housing, end caps, external insulation, internal piping (for solid transfers and gas distribution), short-term storage vessels and particulate filters on a bare cost basis, and then applied a factor (115% of the bare material cost) for installation and delivery. Cost of the sorbent reactors is estimated to be $369,423.

6.4 Sorbent Inventory Costs

The sorbent cost and the sorbent life (i.e., mercury absorption capacity of the sorbent) are the two determinants of the sorbent replacement costs. Since the sorbent will be eventually expended after many cycles, low sorbent cost is critical to cost-effective removal of the contaminants. Although we select inexpensive sorbent precursors, the fabrication costs constitute a large fraction of the cost of the final sorbent (usually 50-60% of the sorbent cost). We anticipate that sorbent can be manufactured at a cost approximately $5/lb, based on a preliminary estimate provided by Saint Gobain NorPro Corporation. This includes the cost of materials as well as the fabrication costs.

Table 19. Cost of sorbent reactors.

Cost of Reactor Vessel			
Volume		145.0	ft^3
Height		2.9	ft
Diameter		8.0	ft
Aspect Ratio		4.35	
Thickness		0.375	in
Volume Steel		2.27	ft^3
Density Steel		487	lb/ft^3
Weight Steel		1104.9	lb
Cost/lb of Steel		3.0	$/lb
Cost of Reactor Shell	$	3,315	
Endcaps	$	7,292	
Bare Module Cost	$	10,607	

Insulation			
Height		3.71	ft
Diameter		120	in
Thickness		4	in
Volume of Mat.		37.56	ft^3
Density St		6.2	lb/ft^3
Weight St		232.8	lb
Cost/lb St		20	$/lb
Insulation Cost	$	4,657	

Reactor Auxiliary Equipment		
Sorbent Trays	$	10,057
Internal Tubing/Distributers	$	12,571
In-House Porous Steel Filters	$	1,200
Sorbent Storage Vessels	$	7,955
Auxiliary Equipment Cost	$	23,829

Reactor Cost		$	39,092
Labor for Installation	110% of reactor cost	$	43,002
Installed Reactor Costs		$	82,094
Cost of 3 Identical Reactors		$	246,282
Piping/Valves/Controls	50% of installed reactor cost	$	123,141
Cost of Reactors		$	369,423

We calculated the cost of the sorbent required during the process start-up. In the analysis, we calculated the volume of the sorbent required in each reactor and the amount retained in the short-term storage vessels (assuming a snapshot of continuous operation). Estimating the packing density of the pellets in these locations and the density of the sorbent itself, we identified the amount of sorbent required as start-up inventory. Based upon the reactor volume 435 ft^3 (3x145), the sorbent amount required is estimated as 25,320 lb (i.e., sorbent density is 58 lb/ft^3) for the initial charge-up. The total initial capital investment in the sorbents is estimated about $126,150.

6.5 Cost of the Circulation Fan

The process uses an electric fan to circulate the gases in the circulation loop. The fan also provides enough pressure head to compensate for the pressure drop in the process equipment in the regeneration loop (i.e., the pressure drop through the two sorbent beds and heat

exchange equipment). In the analysis, we first calculated the density of the gases to be compressed at the inlet conditions. We then estimated the volumetric gas flow rate at the inlet of the fan to be used in the cost equation. The electric fan cost is calculated by the equation presented below provided by Icarus Cost Estimating Software:

$$\text{Fan Cost} = 22344 * \text{ACFM}^{-0.5462} / \text{ACFM}$$

The cost of the circulation fan is estimated to be about $22,462 (Table 20).

Table 20. Cost of circulation fan.

Stream Properties		
Molar Flow	418.6	kmol/h
Temperature	245	C
Pressure	1.2	atm
Volumetric Flow	247,245	alm
Cost Estimation		
Flow Rate	8736.6	acfm
Pressure Head	2.0	psi
Mass Flow	9682.0	lbm/hr
Cost / lbm flow	2.32	$ / lbm/hr
Cost of Fan		**$ 22,462**

We also calculated the power requirement for the desired compression. In the calculation, we assumed gas properties in the proximity of diatomic gases and the fan operating with 80% isoentropic efficiency. The power requirement for the compression is calculated slightly below 36 kW. During the compression stage, some of the power supplied to the compression will be lost heating up the process gases. We estimated a 12°C temperature increase based upon the efficiency used the fan design. This increase will compensate for some of the heat losses in the circulation loop and bring the temperature of the gases under circulation to desired levels to be used in the regenerating bed.

Table 21. Power requirement for gas circulation.

Power Requirement			
P1	15.0	psi	2160 lbf/ft2
P2	17.0	psi	2448 lbf/ft2
kappa	1.4		
q	8,737	cfm at the inlet cond.	
Ns	1	compression stages	
Power	72.9	hp	
	54.3	kW	
Isoentroic efficiency	0.8		
Power Requirement			**67.9 kW**
Cost of Power @	**3.5**	**cent/kWh**	**$16,640**

6.6 Heat Exchangers

In the process schematic, we used one recuperative heat exchanger, one air cooler and a steam heater. Based upon the energy balance across each unit, we calculated the heat duty involved in each heat exchange operation. We designed the heat exchangers as counter flow devices. Based upon the temperatures of the inlet and outlet streams for the hot and cold fluids, we estimated the logarithmic mean temperatures for each unit (Table 22). We used correlations to estimate the heat transfer coefficients. We then used the heat transfer equation given below to calculate the heat exchange area needed in each unit:

$$Q = U A \Delta T_{lm}$$

Table 22. Stream temperatures for heat exchangers.

	HEAT EXCHANGER #1		GAS COOLER #1		GAS HEATER #1	
	oC	oF	oC	oF	oC	oF
T_hi	260	500	130	266	400	752
T_co	245	473	50	122	290	554
T_ho	130	266	120	248	380	716
T_ci	120	248	35	95	260	500
		Btu/h		Btu/h		Btu/h
Heat Duty		1,510,440		116,188		290,469

After calculating the minimum heat exchange area, we added a 15% safety factor to size the units. We selected a construction material based upon the operation temperature. We used

shell and tube configuration as the basis of our calculation. We used the following equations for each type of steel to determine the cost per unit heat exchange area (i.e., $/ft^2).

Stainless Steel 600 psi, 1500°F	Cost = 653.21 * Area$^{-0.3973}$
Stainless Steel 600 psi, 1200°F	Cost = 558.74 * Area$^{-0.3832}$
Carbon Steel 600 psi, 900°F	Cost = 495.45 * Area$^{-0.4276}$

Table 23 lists the specifications and costs for each heat exchange units. These cost factors are then multiplied with the heat exchange area to determine the overall cost, including the labor and installation.

Table 23. Heat exchanger specifications.

	HEX #1	COOLER #1	HEATER #1
Delta T_{lm}	22.2	148.5	206.9
Q (Btu/hr)	1,510,440	116,188	290,469
A (ft2)	12601.5	144.9	166.3
U (Btu/h F ft2)	5.94	5.94	9.29
Cost	$ 176,959	$ 5,528	$ 14,858
$/ft^2	11.76	31.9	74.84
Tmax (oC)	260	130	400
Material of Construction			
Shell-side	A285	A215	A285
Tube-side	A285	A215	SS304

Total Cost of Heat Exchange Equipment	**$ 197,346**

6.7 Capital Investment Requirement

Based upon the installed equipment costs, we calculated the capital investment requirement for the overall system based upon year 2002 values. We estimated the total capital requirement as approximately $1.325 million dollars. Table 24 summarizes the costs involved with the capital items. We assumed a 30% cost for the facilities and a 2-month allowance in early design for the working capital.

Table 24. Total capital requirement.

DIRECT COSTS SUMMARY (2002 PRICES)	Equipment	Labor	Total
Sorbent Reactors	369.4	7.4	376.9
Heat Exchange Equipment	197.3		197.3
Gas Circulation Equipment	22.5		22.5
Sorbent Storage/ Transfer Equipment	73.0		73.0
TOTAL DIRECT COSTS	**662.2**	**7.4**	**669.7**
INDIRECT COSTS (Percentage of direct labor)		50%	3.7
TOTAL DIRECT AND INDIRECT COST			**673.4**
ENGINEERING (percentage of direct costs)		5%	33.7
OVERHEAD & ADMINISTRATION (percentage of direct costs)		8%	53.9
CONTINGENCY		18%	121.2
FEE (percentage of on-site costs)		5%	33.7
TOTAL PLANT COST			**915.8**
STARTUP COST (percentage of direct costs)		3%	20.1
SPARE PARTS (percentage direct equipment costs)		5%	33.1
INITIAL SORBENT/ CHEMICALS INVENTORY			126.2
FACILITIES		30%	202.0
LAND		see note	0.0
WORKING CAPITAL (2 months of annual operating cost)			28.7
TOTAL CAPITAL REQUIREMENT			**1325.9**

Note - Cost of land is not included

6.8 Operating and Maintenance Expenses

The operating and maintenance costs are presented in Table 25. These expenses include labor and supervision costs, and maintenance labor and supplies. Due to the similarities between these systems, we used the labor costs as indicated by Rutkowski and coworkers and applied the same fractions as they used in their analysis for supervision.

Table 25. Operating and maintenance expenses (2002 prices).

PLANT PARAMETERS				
Plant net capacity, MW				250
Hg level before removal, ppbw				52.0
Hg level after removal, ppbw				5.0
Capacity factor				80%
Hg removed, lbs/year				130.50
Sorbent loading, %wt.				0.92%
CAPITAL COST ($)				
Total Capital Costs (TCC)			$	1,325,863
TCC, $/kW				5.30
OPERATING & MAINTENANCE COSTS ($/year)				
Operating labor*			$	4,380
Supervising labor*			$	657
Maintenance labor*			$	2,409
Maintenance material		1% of TCC	$	13,259
Sorbent replacement cost			$	70,924
Sorbent replacement		14,185		
Sorbent Cost, $/lb		5.00		
Sorbent Disposal Costs			$	3,546
Disposal cost, $/ton		500		
Power Costs			$	31,357
Fan power for gas circulation	$	16,640		
Compensate for pressure drop	$	14,717		
Overhead			$	12,423
Taxes, insurance and admin. costs		4% of TCC	$	53,035
Total O&M Costs			**$**	**191,989**
Capital recovery cost			$	198,879
Capital recovery factor		15%		
Total annual costs			$	390,868
Cost of Mercury Removal, $/lb			**$**	**2,995**

** same as Rutkowski et al., 2002*

Operating labor: 1 hour/shift @ $20/h
Supervision: 15 percent of the operating labor
Maintenance costs: 0.5 hour/shift @ 10% wage premium over labor wage
Power cost: Using 4 psi pressure drop and 35 mills per kWh
Overhead Costs: 60 percent of operating labor and maintenance costs

We also estimated other cost items for our process such as the sorbent replacement cost, sorbent disposal cost, power costs, as indicated in Table 25. We estimated the sorbent replacement frequency and associated costs based upon the performance of the sorbent used in the high temperature beds using the result of the experiments; an overall absorption capacity of 0.92% wt. Annual sorbent replacement cost and the disposal cost is estimated as $70,924 and $3,546 (based upon $500/ton of hazardous material removal cost), respectively.

We then calculated the levelized cost of capital (i.e., capital recovery cost) over the unit quantity mercury removed based upon TDA's process using a 15% fixed charge rate. The cost of capital recovery is added to the O&M expenses to calculate the annualized cost for the mercury removal system. Dividing this value to the annual amount of mercury removed, we estimated the cost of removal of mercury as $2,995/lb (2002 prices).

Our mercury costs are far lower than those for pulverized coal combustion power plants. A recent DOE study predicts that the cost of removal of mercury from pulverized coal combustion plants ranges from $4,000 to up to $37,000 per lb of mercury removed with activated carbon injection. This large range depends on the plant/coal type and to the consideration of the impact of activated carbon on the by-product fly ash (Many coal plants sell fly ash as a cement extender. The fly ash contaminated with carbon may have no sale value further it becomes a waste to be disposed).

6.9 Impact of Efficiency

Previous studies based on low temperature adsorbents estimated the cost of removal of mercury from coal-derived synthesis gas as $3,412/lb. Considering the highly preliminary nature of our analysis, we believe that these cost figures are essentially identical. Our sorbent system has much lower sorbent replacement costs but higher capital costs, while their design philosophy incurs high contact times and higher sorbent costs (but low hardware cost). However, the major cost of impact of our system is related to its high temperature operation. To demonstrate this effect, we carried out the following calculation. Based upon a cost of electricity value of 35 mills/kWh and an estimated efficiency loss caused by reduced operating temperature to carry out mercury removal, we estimated an annual cost for the efficiency loss.

There are two major causes for the efficiency loss in the IGCC plant, one is related to reducing the fuel gas temperature. More fuel needs to be burned to achieve the turbine operation temperature due to the low inlet gas temperatures and the electricity produced per fuel fed to the system will be reduced. In addition, more losses will occur when the steam in the synthesis gas is condensed. Steam may constitute up to 64% of the coal gas following the quench step and its condensation takes significant energy from the fuel gas and reduces the mass throughput to the gas turbine. Depending on the type of the gasifier this loss can be quite high. Using a representative number for the efficiency loss (we assumed that around 10% of the efficiency value that can be achieved by the IGCC will be lost). Depending upon the type of the application this cost can be quite high. For 250 MW power plant used in the analysis, this translates into a power cost of $6,125,000, in addition to the cost figure of $445,000 estimated by the Parson's analysis, the overall cost impact of low temperature mercury removal increases to approximately 6.6 million, in comparison to $390,000 estimated for our sorbent system. Based upon this criterion, our system can be 10 to 15 times more expensive and still can be more attractive than a low temperature removal system.